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A REVIEW OF CHEMICALLY REACTIVE PLUME MODELS. PART II. MODELS INCORPORATING MICRO- AND MACRO-MIXING PROCESSES

This two-part article presents chemically reactive plume models which describe the formation of secondary pollutants in plumes emitted from tall stacks. The models are classified according to the way they treat turbulent mixing processes. The term *turbulent mixing* involves here both macro-mixing and micro-mixing. *Macro-mixing* processes account for the variation of mean concentrations, while *micro-mixing* processes account for the deviations from the mean values. Part I presents the models, in which only the macro-mixing processes are taken into account. Part II is devoted to the models, which either focus on the micro-mixing processes only or account for both the macro- and micro-mixing processes.

1. INTRODUCTION

In this review, chemically reactive plume models, which describe the transport, dispersion and non-linear chemistry of plumes emitted from high-level point sources, are classified according to the way they treat mixing processes [21], [22]. The term *mixing processes* involves here both macro-mixing and micro-mixing [7], [10]. *Macro-mixing* is related to the expansion of plume as a whole and mixing of the ambient air with stack effluents inside a plume at a level of mean concentrations. *Micro-mixing* is related to small fluctuations of concentrations, i.e. fluctuations in excess of or below average values.

In part I of this article, the models, in which only macro-mixing processes are taken into account, have been described [34]. Four classes of these models are distinguished:

- class "1": uniformly-mixed expanding-volume models,
- class "2": partially-perfectly-mixed expanding-volume models,
- class "3": sectionally-homogeneous expanding-multi-volume models,
- class "4": extended Gaussian type models.

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Part II of this article is devoted to the models, which either focus only on micro-mixing processes or account for both macro- and micro-mixing processes. The above four classes of macro-mixing models are supplemented with the following models incorporating micro-mixing processes:

- class "5": concentration fluctuations models,
- class "6": models which account for main gradients and concentration fluctuations,
- class "7": probability density function (p.d.f.) models,
- class "8": large eddy simulation (L.E.S) models.

The models described in part II have some common features which are summarised below.

In the models incorporating macro-mixing and micro-mixing processes a term describing the chemical transformations of the species i which undergoes the bimolecular non-linear reaction with the species k of the type:



takes the following form:

$$\bar{R}_i = -k_r \overline{C_i C_k} = -k_r \bar{C}_i \bar{C}_k - k_r \overline{C'_i C'_k}, \quad (1)$$

where \bar{R}_i is the chemical reaction term; k_r is the chemical reaction rate coefficient; \bar{C}_i and \bar{C}_k are the mean concentrations of the species i and k , respectively; $\overline{C'_i C'_k}$ is the concentration fluctuations' co-variance. The concentration fluctuations' co-variance increases an absolute value of the overall rate of reaction if reactants are premixed and decreases this value if they are not premixed [10].

The micro-mixing processes should be taken into account in the models in case of moderate and fast chemistry. The division of chemical reactions into three groups: slow, moderate and fast chemistry is based on the value of a parameter called the Damkeler number. The Damkeler number D is defined as the ratio of characteristic time scale of turbulence to that of chemical reactions. Using this parameter one can establish the following classification [20]:

- slow chemistry ($D \ll 1$),
- moderate chemistry ($D \cong 1$),
- fast chemistry ($D \gg 1$).

In the case of slow chemistry, turbulence is capable of mixing reactants before any significant reaction takes place. For moderate chemistry, the chemical transformation is controlled by the way in which reactants are introduced, i.e. premixed and not premixed, and by the capacity of the turbulence to mix chemical species. For fast chemistry, chemical species are transformed as soon as the turbulence bring them together, i.e. the reaction is diffusion-controlled and it takes place only at the interface between parcels containing reacting species [10], [20], [29].

In addition to the Damkeler number, the intensity of segregation I_s is the adequate estimator of the state of mixing of two not premixed species. I_s is defined as a covariance between the concentration fluctuations of two chemical species normalised by products of their means:

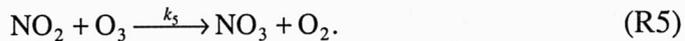
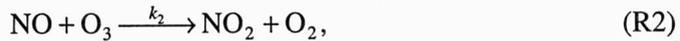
$$I_s = \frac{\overline{C_i' C_k'}}{\overline{C_i} \overline{C_k}}. \quad (2)$$

It takes the following limiting values: $I_s = 0$ in the case of perfect mixing (this occurs for slow chemistry) and $I_s = -1$ in the case of complete segregation (this occurs for fast chemistry; reactions take place only at the interfaces of reactants) [8], [20].

The chemical term, after introducing the intensity of segregation, takes the following form:

$$\overline{R_i} = -k_r \overline{C_i} \overline{C_k} (1 + I_s). \quad (3)$$

In the models of classes "5"–"8" the NO–NO₂–O₃ chemical system is considered. This is one of the most important cycles in the atmosphere. In order to keep the chemistry as simple as possible hydrocarbons are not included in the system. The following chemical reactions can be included in the NO–NO₂–O₃ chemical system [10]:



The chemical reaction (R2) is the oxidation of nitric oxide by ozone. The reaction (R3) is the photodissociation of nitrogen dioxide by solar radiation. The chemical coefficient k_3 is a function of the light intensity. The reaction (R4), i.e. the oxidation of NO by O₂, is too slow at typical ambient NO concentrations to be significant. It may occur for a brief period in plumes when NO concentrations are high. It takes place as plumes escape from stacks before significant dilution with the surrounding air has occurred. The reaction (R5) is important only under nocturnal conditions when the reaction (R4) is excluded. As a consequence, during day time in most of the models the chemical cycle NO–NO₂–O₃ can be described by the reactions (R2) and (R3). In the extreme case, only one (the most important) reaction (R1) is studied in isolation.

Unless it is stated otherwise, in the models described in this review a Cartesian coordinate system fixed to the ground is used.

Four distinguished classes of chemically reactive plume models, which are either focused on micro-mixing processes or account for macro- and micro-mixing proc-

esses, are described in the succeeding sections. For each class main assumptions and basic mathematical equations are presented. Applications and the tests carried out are discussed. In the final section, some conclusions and remarks related to modelling of turbulent, chemically reactive flows in the atmospheric boundary layer are formulated.

2. CLASS "5": CONCENTRATION FLUCTUATIONS' MODELS

Models included in this class are focused on micro-mixing processes. They account for concentration fluctuations assuming homogeneous mean concentration fields in a control volume of the atmosphere.

Two types of models falling into this class were found in the literature:

- models in which co-variances of fluctuation concentrations are incorporated by means of the "concentration field splitting" technique [31], [42],
- models in which the fluctuation concentrations' co-variances are incorporated by means of the "probability density of conserved scalar" approach [3], [26].

2.1. MICRO-MIXING MODELS BASED ON THE "PROBABILITY DENSITY OF MIXING SCALAR" APPROACH

A model of BILGER [3] concerns the mixing of nitric oxide-rich emissions with ozone-rich background air. It refers to a system comprising a macroscopically mixed atmospheric volume, where mean concentrations are uniform. A basic concept in the model is a mixture fraction ζ defined as the fraction of the local mixture which originates from NO-rich emissions. A remaining fraction $(1 - \zeta)$ is that originating from the old O₃-rich air. It is assumed that: (i) the NO₂-O₃-NO chemical system is described by reactions (R2) and (R3); (ii) the photostationary state relation holds pointwise and instantaneously.

The model of Bilger is based on three instantaneous equations: two equations for conserved sums of nitrogen oxides and total oxidants and the photostationary state equation. They are as follows:

$$[\text{O}_3] + [\text{NO}_2] = \zeta \{ [\text{O}_3]_1 + [\text{NO}_2]_1 \} + (1 - \zeta) \{ [\text{O}_3]_2 + [\text{NO}_2]_2 \}, \quad (4)$$

$$[\text{NO}] + [\text{NO}_2] = \zeta \{ [\text{NO}]_1 + [\text{NO}_2]_1 \} + (1 - \zeta) \{ [\text{NO}]_2 + [\text{NO}_2]_2 \}, \quad (5)$$

$$\frac{[\text{O}_3][\text{NO}]}{[\text{NO}_2]} = \frac{k_3}{k_2}, \quad (6)$$

where $[\varphi]$ denotes the instantaneous pointwise concentration of the species φ ; $[\text{O}]$ is neglected because its value is small compared to the values of $[\text{O}_3]$ and $[\text{NO}_2]$; the subscripts 1 and 2 refer to the fresh NO-rich emissions and the old O₃-rich air, respectively.

Normalising the system of equations by $[\text{NO}_2]_2 + [\text{O}_3]_2$ yields:

$$Y + Z = \omega\beta\zeta + (1 - \zeta), \quad (7)$$

$$X + Y = \beta\zeta + \nu(1 - \zeta), \quad (8)$$

$$\frac{XZ}{Y} = \kappa = \frac{k_1}{k_3\{[\text{O}_3] + [\text{NO}_2]\}}, \quad (9)$$

where

$$\omega = \{[\text{O}_3]_1 + [\text{NO}_2]_1\} / \{[\text{NO}]_1 + [\text{NO}_2]_1\},$$

$$\nu = \{[\text{NO}]_2 + [\text{NO}_2]_2\} / \{[\text{O}_3]_2 + [\text{NO}_2]_2\},$$

$$\beta = \{[\text{NO}]_1 + [\text{NO}_2]_1\} / \{[\text{NO}_2]_2 + [\text{O}_3]_2\}.$$

The system of equations is solved with respect to normalised instantaneous pointwise concentrations of NO, NO₂ and O₃, i.e. with respect to X, Y and Z in terms of a new parameter $\xi = \beta\zeta$. Reducing the term $(1 - \zeta)$ to 1 since $\zeta \ll 1$ and taking ω , ν and κ as given constants, one obtains:

$$X = \frac{1}{2}\{(1 - \omega)\beta\xi - 1 + \nu - \kappa + \sqrt{U}\}, \quad (10)$$

$$Y = \frac{1}{2}\{(1 - \omega)\xi + 1 + \nu - \kappa - \sqrt{U}\}, \quad (11)$$

$$Z = \frac{1}{2}\{-(1 - \omega)\xi + 1 - \nu - \kappa + \sqrt{U}\}, \quad (12)$$

where

$$U = [1 + \kappa - \nu - 1 - (1 - \omega)\xi]^2 + 4\kappa(\xi + \nu).$$

Average concentrations of reactive species are obtained by weighting the instantaneous pointwise concentrations with a probability density function (p.d.f.) for ξ , $p(\xi)$:

$$\bar{X} = \int_0^{\infty} X(\xi)p(\xi)d\xi, \quad (13)$$

$$\bar{Y} = \int_0^{\infty} Y(\xi)p(\xi)d\xi, \quad (14)$$

$$\bar{Z} = \int_0^{\infty} Z(\xi) p(\xi) d\xi, \quad (15)$$

$$p(\xi) = (1 - \gamma) p^n(\xi) + \gamma p'(\xi), \quad (16)$$

where γ is the intermittency, $p^n(\xi)$ is the p.d.f. in the outside uncontaminated fluid and $p'(\xi)$ is the p.d.f. in the mixing, turbulent, contaminated fluid. The form of p.d.f. is obtained based on the results of atmospheric and laboratory experiments [3], [4].

The model of Bilger was used to study the nature of the NO-NO₂-O₃ photostationary state when freshly emitted NO_x admixed with a photochemical smog. The main features of the results agree qualitatively well with field observations. The values of the photostationary state ratio [NO][O₃]/[NO₂] greater than unity probably arise from both of two mechanisms considered. They are the following: inhomogeneities in composition during mixing of freshly emitted NO_x with a smog giving high values through the averaging process; and disturbance of the quasi-equilibrium due to high rates of diffusional mixing of ozone with fresh nitric oxide. Both mechanisms are favoured by low intensity of ultraviolet light, intermittent and high-intensity turbulent fluctuations as well as background smog of high ozone and low NO_x concentrations.

In order to explain the decrease of the photostationary state ratio [NO][O₃]/[NO₂], which becomes smaller than unity, KEWLEY [26] applies governing equations (7)–(9) from the model of Bilger to the case when the clean air mixes with the smog. In the model of Kewley, ζ is a fraction of the local mixture which originates from the clean air, consequently $(1 - \zeta)$ is a fraction which originates from the O₃-rich air. In this case $\beta \ll 1$, therefore ζ is incorporated in equations (7)–(9), but the terms with β are omitted and equations (7)–(9) simplify to:

$$Y + Z = 1 - \zeta, \quad (17)$$

$$X + Y = \nu(1 - \zeta), \quad (18)$$

$$\frac{XZ}{Y} = \kappa. \quad (19)$$

The solution with respect to X , Y , Z in terms of ζ is given by:

$$X = \frac{1}{2} \left[-(1 - \zeta)(1 - \nu) - \kappa + \sqrt{U} \right], \quad (20)$$

$$Y = (1 - \zeta)\xi - X, \quad (21)$$

$$Z = (1 - \zeta) - Y, \quad (22)$$

where

$$U = [(1 - \zeta)(1 - \nu) + \kappa]^2 + 4\kappa\nu(1 - \zeta).$$

Averages of reactive species are expressed by equations (13)–(15) with p.d.f. for ζ given by equation (16).

The model of Kewley was applied to predict the photostationary state ratio of $[\text{NO}][\text{O}_3]/[\text{NO}_2]$ in the case when clean air mixed with a smog. The results show that this parameter can be smaller than unity, especially when no mixing effects occur and small amounts of smog mix with a background air. A minimum value in this case is expected under the following conditions: the high intensity of ultraviolet light, intermittent and low intensity of turbulent fluctuations and low NO_x concentrations. The work of Kewley complements the work of Bilger so that the oscillations of the photostationary state ratio $[\text{NO}][\text{O}_3]/[\text{NO}_2]$ between the values higher or lower than unity can be given explanations.

2.2. A MICRO-MIXING MODEL BASED ON THE "CONCENTRATION FIELD SPLITTING" TECHNIQUE

A mathematical basis for a model of Shu and co-workers [31], [42] is the transport-diffusion chemical equation averaged for the space over a plume cross-section. The transport-diffusion chemical equation for cross-sectionally averaged concentrations does not need closure of turbulent fluxes. Closure with respect to the chemical term, which includes both mean concentrations and fluctuations of concentrations, is achieved by the "concentration field splitting" technique. Details about the derivation of this equation are discussed in the original paper [31]. Below only assumptions and the way of closure of equation are described.

It is assumed that: (i) there is a mean wind along the x -axis and no variation of wind with a height; (ii) the molecular diffusion is neglected; (iii) the turbulent diffusion along the x -axis is neglected; (iv) there is no other production–reduction terms than chemical reactions; (v) the mean concentration fields are constant in time.

The governing equation for the cross-sectionally averaged concentration of the species i has the following form:

$$\bar{u} \frac{d\bar{C}_i}{dt} = \bar{R}_i, \quad (23)$$

where \bar{u} is the mean wind velocity; \bar{C}_i is the spatially averaged concentration; the volume s , over which it is averaged, consists of the assemble of plume cross-sections bounded by $-L_y \leq y \leq L_y$ and $0 < z \leq L$ at the distance x from the source; L_y is the distance large enough that the spread of the plume in the y -direction does not exceed L_y for all values of x ; L is the height of the mixing layer; \bar{R}_i is the chemical term.

In the model of Shu and co-workers, the closure of the chemical term \bar{R}_i covers the case of two reactive species: i and k undergoing the bimolecular non-linear reac-

tion (R1). The approximation is obtained by introducing chemically inert "surrogates" of reactants and next by splitting concentrations of reactants and surrogate species into two components whose evolution, statistical moments and correlations are more easily predictable than those of reactant concentrations. This method is called the "concentration field splitting" technique [21], [22]. It allows us to break up the chemical term into number of terms several of which are independent of chemistry. The following expression is obtained:

$$\overline{R_i} = -k_r \overline{C_i C_k} = \frac{-k_r}{\mu_i \mu_k} \eta M_{i,k}^{in} \left(\overline{C_i} - (1 - \mu_i) \overline{C_i^{in}} \right) \left(\overline{C_k} - (1 - \mu_k) \overline{C_k^{in}} \right), \quad (24)$$

where k_r is the chemical reaction rate coefficient; η is the reaction parameter; μ_i, μ_k are the mixing parameters; $M_{i,k}^{in}$ is the mixing function of the inert species i and k ; $\overline{C_i}, \overline{C_k}$ are the concentrations of reactive species averaged over the plume cross-section; $\overline{C_i^{in}}, \overline{C_k^{in}}$ are the concentrations of the surrogate species. The concentration fields of surrogate species represent the concentration fields of reactants, which would exist if reactants did not react with each other.

This is a complex task to estimate the parameters in the above equation for a general case. A substantial simplification of equation (24) can be obtained in the case of point release of the species i in the initially uniform field of the species k and provided that the concentrations of the species i at least near the plume axis are much greater than the background concentrations of the species k . Then the following approximations are valid:

$$\eta = 1, \quad \mu_i = 1, \quad \mu_k = \frac{\overline{C_i^{in} C_i^{in}}}{\overline{C_i^{in}} \overline{C_i^{in}}}, \quad M_{i,k}^{in} = 1. \quad (25)$$

The quantities μ_k in the model of Shu and co-workers are calculated based on the studies of LAMB [30] and data generated by a numerical planetary boundary layer model of DEARDORF [11], [12]. They are derived for specific emission and meteorological conditions and are not necessarily independent of source area, nor are applicable to release heights other than $h = 0.1L$. Further study is needed to investigate how the mixing parameter μ_k depends on emission and meteorological conditions.

The model of Shu and co-workers was tested for the NO-NO₂-O₃ system by simulating the rate of nitric oxide oxidation in a near-source portion of plume from the Potomac Electricity Company power plant at Morgantown, Maryland, USA. The results agree with the observations and indicate that turbulent concentration fluctuations greatly inhibit the rate of nitric oxide conversion in a plume for a period of about $2L/w^*$. For the conditions studied, i.e. $L = 1000$ m, $w^* = 1.8$ m/s, this period of time lasts for about 20 minutes. When fluctuations effects are eliminated from the model in

one particular case, the time of 50% conversion of NO into NO₂ reduces from 20 minutes to about 3 minutes.

The calculations indicate that turbulent fluctuations are essential in the chemical conversion in a near-source plume and should be considered in the prediction of atmospheric plume chemistry.

3. CLASS "6": MODELS WHICH ACCOUNT FOR MEAN GRADIENTS AND CONCENTRATION FLUCTUATIONS

Models included in this class account for both inhomogeneous fields of mean concentrations and concentration fluctuations. The following models are described here:

- multi-ring models in which micro-mixing processes are incorporated by means of either the results of wind tunnel experiments [7] or a simplified second-order closure model of de ARELLANO and DYUNKERKE [10], [20],

- numerical, classical *K*-theory models in which micro-mixing processes are incorporated by means of one of the following techniques: the "probability density of conserved scalar" approach [26], [27], an "inter-diffusion model" of PATTERSON [37], [25], or an "interaction by exchange with a mean (I.E.M.) model" of VILLERMAUX [13], [17], [46],

- numerical, modified *K*-theory model in which micro-mixing processes are incorporated by means of the "concentration field splitting technique" of SHU and LAMB [21], [22], [42].

3.1. A MULTI-RING MODEL IN WHICH MICRO-MIXING PROCESSES ARE INCORPORATED BY MEANS OF THE RESULTS OF WIND TUNNEL EXPERIMENTS (CO-VARIANCES PRESCRIBED AS A FUNCTION OF AVERAGE CONCENTRATION VALUES OBTAINED ON THE BASIS OF THE RESULTS OF WIND TUNNEL EXPERIMENTS)

A model of de ARELLANO and co-workers [7], [10] can be considered as the development of multi-ring models described in part I of this article [34]. Macro-mixing processes are described in all multi-ring models in the same way. The difference between the models lies in the treatment of micro-mixing processes. In the models described in part I of this article concentration fluctuations are neglected, while in the model of de Arellano and co-workers the concentration fluctuations are taken into account. They are described using empirical expressions.

Macro-mixing in all multi-ring models is taken into account by dividing an elliptical plume into concentric elliptical rings. Change of material between the rings and the entrainment of the ambient air to the outermost ring are allowed. The mass-balance equation for the specific species *i* for the ring number *j* has the following form:

$$\frac{d\bar{C}_i^j}{dt} = f \left(l_i \bar{C}_i^{j-1} + m \bar{C}_i^j + n \bar{C}_i^{j+1} \right) + \bar{R}_i^j, \quad (26)$$

where: f is the parameter calculated as the function of the product of Gaussian dispersion coefficients δ_y and δ_z ; l, m, n are the parameters calculated as the functions of the ring index j and the total number of rings N ; \bar{R}_i^j is the change of pollutant concentration due to chemical reactions.

In the macro-mixing models the chemical term present in this equation for the case when two species: i and k undergo the bimolecular non-linear reaction (R1) has the following form:

$$\bar{R}_i = -k_r \bar{C}_i \bar{C}_k, \quad (27)$$

where k_r is the reaction rate coefficient; \bar{C}_i, \bar{C}_k are the mean concentrations of the species i and k , respectively.

In the model of de Arellano and co-workers, a correlation term of concentration fluctuations $\overline{C'_j C'_k}$ is additionally included in the chemical term, and equation (1) is used to describe chemical reactions between the species i and k .

In the model of de Arellano and co-workers, only the NO-NO₂-O₃ system is considered and reactions (R2)-(R5) are taken into account. The calculated mean concentrations refer to time averages. The plume dispersion parameters δ_y and δ_z in equation (26) are calculated using the hourly averages. The set of mass balance equations is solved for each of species of the chemical system. In order to close the chemical term, the co-variances of $\overline{NO'NO'}$ and $\overline{NO'O_3}$ should be described. The micro-mixing related to the fluctuations of nitric oxide ($\overline{NO'NO'}$) is modelled using the formulation of the inert species proposed by WILSON et al. [47]. Micro-mixing related to fluctuations of nitric oxide and ambient ozone ($\overline{NO'O_3}$) is modelled using the results obtained in the wind tunnel experiments carried out by BULTJES [4] and field data gathered by FRANK et al. [18] (TUV-Essen). The concentration co-variances are kept constant across a plume and are described only as a function of the average concentrations' values, atmospheric stability and downwind distance.

The model of de Arellano and co-workers was validated based on the data obtained during different emissions and under different meteorological conditions [28]. A plume was traced up to 20 km from a stack. The results show that under diurnal neutral conditions the calculated and observed NO₂/NO_x ratios are in a close agreement. A similar agreement was obtained under stable nocturnal conditions when photodissociation of NO₂ did not occur. Of the concentration fluctuations included in the model, the $\overline{NO'O_3}$ term is more important than the $\overline{NO'NO'}$ term and its influence spreads across 10 km (neutral atmospheric conditions) after the NO_x release. The $\overline{NO'O_3}$ term produces the retardation in the conversion of NO to NO₂. In daytime, this effect is reflected both in the measurements and model calculations in all cases studied except one.

3.2. A MULTI-RING MODEL IN WHICH MICRO-MIXING PROCESSES ARE INCORPORATED BY MEANS OF A SIMPLIFIED, SECOND-ORDER CLOSURE MODEL OF DE ARELANO AND DUYNKERKE (CO-VARIANCES DERIVED FROM THEIR TRANSPORT EQUATIONS)

A model of GALMARINI and co-workers [20] also belongs to the group of multi-ring models. The macro-mixing in such models is described by equation (26). Micro-mixing is incorporated into this model by means of a one-dimensional, simplified, second-order closure model of de ARELANO and DUYNKERKE [10]. This allows us to calculate explicitly the concentration variations of chemically reactive species.

The model of Galmarini and co-workers describes the NO-NO₂-O₃ chemical cycle applying reactions (R2) and (R3). It simulates a release of pollutants under neutral atmospheric conditions. Concentration fields of NO, NO₂ and O₃ are calculated using the following procedure:

1. The concentration field for the inert component NO_x defined by NO_x = NO + NO₂ is calculated based on the mass balance equation (26) with the chemical term being omitted.

2. The concentration fields of NO and NO₂ species resulting from plume dispersion are obtained, provided that the initial proportions of NO/NO_x and NO₂/NO_x are known.

3. The ozone concentration field due to entrainment caused by plume dispersion is calculated using equation (26).

4. The chemical reactions for NO, NO₂ and O₃ are performed and new values of NO, NO₂ and O₃ are calculated. From these values new ratios of NO/NO_x and NO₂/NO_x are obtained and the calculation of the concentration fields of NO, NO₂ and O₃ proceeds till the next time step and the whole procedure starts again.

In the model of Galmarini and co-workers, the calculated mean concentrations are comparable with ensemble averages. The plume dispersion parameters δ_y and δ_z in equation (26) take the instantaneous values. They are calculated from formulae developed by BANGE et al. [1]. These formulae were obtained by filtering the effect of plume meandering from plume spreading measurements.

In order to describe chemical reactions between NO, NO₂ and O₃, the $\overline{NO'O'_3}$ co-variance should be evaluated. The co-variance $\overline{NO'O'_3}$ is obtained with co-variances of other reactive species by solving a system of variance and co-variance equations of the form:

$$M_{i,k} \overline{C'_i C'_k} = 2K \left(\frac{\partial \overline{C}_i}{\partial r} \right) \left(\frac{\partial \overline{C}_k}{\partial r} \right), \quad (28)$$

where K is the eddy diffusivity whose value is calculated based on the values of plume dispersion parameters δ_y and δ_z ; $M_{i,k}$ is the 6×6 matrix given by:

$$\mathbf{M}_{i,k} = \frac{1}{\tau_i} \begin{bmatrix} 2D_2 + B_{11} & 0 & 0 & 2D_1 & -2D_3 & 0 \\ 0 & 2D_2 + B_{22} & 0 & 2D_2 & 0 & -2D_3 \\ 0 & 0 & 2D_3 + B_{33} & 0 & -2D_2 & 2D_1 \\ D_2 & D_1 & 0 & D_1 + D_2 + B_{12} & -D_3 & -D_3 \\ -D_2 & 0 & -D_3 & -D_1 & D_1 + D_2 + B_{13} & D_1 \\ 0 & -D_1 & -D_3 & -D_2 & D_2 & D_1 + D_2 + B_{23} \end{bmatrix} \quad (29)$$

The first three rows of $\mathbf{M}_{i,k}$ correspond to the variance equations for $\overline{NO'^2}$, $\overline{O_3'^2}$, $\overline{NO_2'}$ and the remaining three – to the co-variance equations $\overline{NO'NO_2'}$, $\overline{O_3'NO_2'}$, $\overline{NO'O_3'}$. The parameter τ_i is the time scale of turbulence; D_1 , D_2 , D_3 are the Damkoler numbers, i.e. the dimensionless time scale ratios between the time scale of turbulence and time scales of specific chemical reactions; B_{ik} are the experimental constants used in the closure of molecular dissipation in the co-variance equation. The variances and co-variances are calculated by inverting the matrix $\mathbf{M}_{i,k}$ and prescribing the values of eddy diffusivities and concentrations gradients of each of species at the interface of rings. The values obtained at this interface are considered to be representative of the inner ring.

The model of Galmarini and co-workers was applied to study the influence of turbulence on a chemical reaction rate. The concentration co-variances, intensity of segregation (I_s) and the Damkoler numbers (D) values, as produced by the model, were studied during the dispersion process.

The values of the downstream I_s show that after the release species tend to be totally segregated and there is no chemical reactions between them. The atmospheric turbulence gradually dilutes the released NO and NO₂ with the ambient ozone, as is shown by the increase of I_s values close to 0. There are different values of I_s in a plume cross-section.

The comparison of the values produced by the model for the Damkoler numbers D_1 and D_2 and for the intensity of segregation clearly shows that D_1 defined as the basis of the time scale of chemistry of NO is sensitive to the various phases of development of the plume dispersion. On the basis of the values of D_1 , the dispersion process can be divided into three different phases: fast, moderate and slow chemistry.

3.3. A CLASSICAL *K*-THEORY MODEL IN WHICH MICRO-MIXING PROCESSES ARE INCORPORATED BY MEANS OF AN "INTER-DIFFUSION MODEL" OF PATTERSON (CO-VARIANCES ARE DESCRIBED ON THE BASIS OF THE VARIANCE OF THE EMITTED SPECIES)

A model of KARAMCHANDANI and PETERS [25] is based on the transport-diffusion chemistry equation with the conventional first-order closure (*K*-theory) for turbulent fluxes. For the correlation term that appears in the chemical rate an empirical "inter-diffusion model" of PATTERSON [37] is used.

The transport-diffusion equation employed in Einstein's summation notation has the following form:

$$\frac{\partial \overline{C}_i}{\partial t} + \overline{u}_\alpha \frac{\partial \overline{C}_i}{\partial x_\alpha} = \frac{\partial}{\partial x_\alpha} \left(K_x \frac{\partial \overline{C}_i}{\partial x_\alpha} \right) + \overline{R}_i + \overline{S}_i, \quad (30)$$

where \overline{C}_i is the time average concentration of the species i ; \overline{u}_α is the average wind speed in the direction x_α ; K_x is the eddy diffusivity in the direction x_α ; \overline{R}_i is the average reaction rate of the species i ; and \overline{S}_i is the average source term for the species i .

The chemical term for the second-order chemical reaction between two species i and k is described by equation (1). The correlation term $\overline{C'_i C'_k}$ is calculated based on the concentration variance $\overline{C'_i C'_i}$ of emitted species by applying the inter-diffusion model of PATTERSON [37] tested in a plug flow reactor:

$$\overline{C'_i C'_k} = -\frac{1-\gamma}{1+\gamma} \overline{C_i'^2}, \quad (31)$$

$$\gamma = \frac{\beta \overline{C}_i \overline{C}_k - \overline{C_i'^2}}{\beta \overline{C}_i \overline{C}_k \overline{C_i'^2}}, \quad (32)$$

where γ represents the degree of inter-diffusion of reactants. When $\gamma = 0$ there is a total segregation, and when $\gamma = 1$ the fluids are perfectly mixed. The limiting values of γ correspond to the limiting values of $(1 - I_s)$, where I_s is defined by equation (1).

The variance equation of emitted species has the following form:

$$\begin{aligned} \frac{\partial \overline{C'_i C'_i}}{\partial t} + \overline{u}_\alpha \frac{\partial \overline{C'_i C'_i}}{\partial x_\alpha} &= \frac{\partial \overline{u_\alpha C'_i C'_i}}{\partial x_\alpha} - 2 \overline{C'_i u'_\alpha} \frac{\partial \overline{C}_i}{\partial x_\alpha} \\ &- 2D_i \left(\frac{\partial \overline{C_i'^2}}{\partial x_\alpha} \right)^2 - k \left(\overline{C}_i \overline{C'_i C'_k} + \overline{C}_k \overline{C'_i C'_i} + \overline{C_i'^2} \overline{C'_k} \right). \end{aligned} \quad (33)$$

The unclosed terms on the right-hand side are modelled using the approximations proposed by WILSON [47], SPALDING [43] and CORRISON [6]. The third-order correlation term $\overline{C_i'^2 C'_k}$ is set zero, which is equivalent to assumption that C'_i and C'_k are symmetrically distributed about \overline{C}_i and \overline{C}_k , respectively. In case of NO-O₃-NO₂ chemical system, the governing equations cover three transport-diffusion chemistry equations for each of the reactive species and the variance equation for NO as the emitted species. The NO-O₃-NO₂ chemistry is described here by reactions (R2) and (R3).

The model of Karamchandani and Peters was used to study the effect of concentration fluctuations on plume dispersion. This effect is shown to be substantial in

a near-source region. The effect is initially magnified with the downwind distance, and then reduced as diffusion and dissipation become dominant. Within a plume itself, the smallest effects are observed at a core of plume and the most pronounced – at its edges. The maximum effect is observed around middays, while the minimal effect is observed early in the morning and late in the evening.

The model of Karamchandani and Peters has been questioned by SEINFELD and GEORGOPOULOS [23] who claim that it is based, to a large extent, on the set of invalid assumptions. They have criticised it for the way of closing the turbulence term (classical *K*-theory) and for adopting some modelling approximations, such as the empirical inter-diffusion model of Patterson, which cannot be applied to an atmospheric point source plume.

3.4. A CLASSICAL *K*-THEORY MODEL

IN WHICH MICRO-MIXING PROCESSES ARE INCORPORATED BY MEANS OF THE "PROBABILITY DENSITY FUNCTION OF CONSERVED SCALAR" APPROACH

The model of KEWLEY [27] can be regarded as the application of the achievements of BILGER [3]. The model is applied to a NO_x stack plume reacting with ozone in a sunny day. It is based on two time averaged equations, i.e. the transport–diffusion equation for the conserved scalar and the balance equation of its variance, and a set of instantaneous equations, i.e. two equations for the conserved sums of nitrogen oxides and total oxidants and the photostationary state relation. The "probability density function of conserved scalar" (p.d.f.) approach is used to obtain average values of reactive species.

It is assumed that: (i) there is a mean wind along the *x*-axis; (ii) the molecular diffusion is neglected in the structure of the overall process; (iii) the turbulent diffusion is negligible in comparison to the mean wind along the *x*-axis; (iv) the concentration field is in a steady state; (v) there is no other volume sources/sinks of the species considered; (vi) reactive pollutants undergo fast enough chemical reactions so that equilibrium is reached.

The transport–diffusion equation for the conserved scalar is closed with respect to the turbulent term with classical *K*-theory. Under these conditions it takes the following form:

$$\bar{u} \frac{\partial \bar{\varphi}}{\partial x} = \frac{\partial}{\partial y} \left(K_y \frac{\partial \bar{\varphi}}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_z \frac{\partial \bar{\varphi}}{\partial z} \right), \quad (34)$$

where φ is the conserved scalar (either φ_1 or φ_2); \bar{u} is the mean wind velocity; K_y, K_z are the horizontal and vertical eddy diffusivities, respectively.

When: (i) the usual order of magnitude is assessed, (ii) the turbulent flux is closed using *K*-theory, (iii) the dissipation term is reduced to the form given by DONALDSON and HILST [14] the balance equation for the variance of conserved scalar takes the following form:

$$\bar{u} \frac{\partial \overline{\varphi'^2}}{\partial x} = \frac{\partial}{\partial y} \left(K_y \frac{\partial \overline{\varphi'^2}}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_z \frac{\partial \overline{\varphi'^2}}{\partial z} \right) + 2 \left\{ K_y \left(\frac{\partial \bar{\varphi}}{\partial y} \right)^2 + K_z \left(\frac{\partial \bar{\varphi}}{\partial z} \right)^2 \right\} - a \overline{\varphi'^2}. \quad (35)$$

The set of instantaneous equations for the NO-NO₂-O₃ chemical system described by reactions (R2) and (R3) is as follows:

$$\frac{[\text{O}_3][\text{NO}]}{[\text{NO}_2]} = \frac{k_3}{k_2}, \quad (36)$$

$$\varphi_1 = [\text{NO}] + [\text{NO}_2], \quad (37)$$

$$\varphi_2 = [\text{O}_3] + [\text{NO}_2], \quad (38)$$

$$\varphi_2 - \varphi_2^a = \frac{(\varphi_1 - \varphi_1^a) Q_1}{Q_2}, \quad (39)$$

where Q_1 , Q_2 are the point source emissions of two conserved scalars, respectively; the superscript a refers to the ambient values of φ .

Based on equations (36)–(39) the concentrations of reactive species are expressed as functions of φ_1 . Once the p.d.f. of φ_1 is known the mean and variance of each species can be found as follows [2]:

$$\overline{[\text{NO}]} = \int [\text{NO}(\varphi_1)] P(\varphi_1) d\varphi_1, \quad (40)$$

$$\overline{[\text{NO}]^2} = \int \{ [\text{NO}(\varphi_1)] - \overline{[\text{NO}]} \}^2 P(\varphi_1) d\varphi_1, \quad (41)$$

where $P(\varphi_1)$ is the p.d.f. of φ_1 .

Based on the review of BILGER [2] devoted to the experimental data gathered for a variety of flows and their application to the atmosphere, typical shapes for the p.d.f. are expected to be Gaussian-like in a centre of a plume and have an intermittency spike at plume edges. The values of $P(\varphi_1)$ are calculated based on the mean $\bar{\varphi}_1$ and the variance $\overline{\varphi_1'^2}$.

The balance equations (37) and (38) can be solved either numerically or analytically, provided that a set of simplifying assumptions is accepted. In the model of Kewley, analytical solutions are used.

The analytical solution of equation (37) is given by:

$$\bar{\varphi} = \bar{\varphi}^a + \frac{\bar{Q}}{2\pi\bar{u}\delta_y\delta_z} \exp\left(-\frac{y^2}{2\delta_y^2}\right) \left\{ \exp\left(-\frac{(z-H)^2}{2\delta_z^2}\right) + \exp\left(-\frac{(z+H)^2}{2\delta_z^2}\right) \right\}, \quad (42)$$

where \bar{Q} is the source strength of $\bar{\varphi}$ at $x = 0$; δ_y, δ_z are the plume dispersion parameters related to the eddy diffusivity coefficients K_y, K_z by the equation of the form: $\delta_\alpha^2 = 2K_\alpha x / \bar{u}$, where $\alpha = y$ or z .

Assuming that the NO_x variance from a stack is negligible compared to that produced in the plume mixing process, the magnitude of $\overline{\varphi'^2}$ is calculated from the equation:

$$\overline{\varphi'^2} = \frac{2}{c} \left\{ K_y \left(\frac{\partial \bar{\varphi}}{\partial y} \right)^2 + K_z \left(\frac{\partial \bar{\varphi}}{\partial z} \right)^2 \right\}, \quad (43)$$

where c is a constant.

The results obtained from the model of Kewley show that for a plume of NO and NO_2 dispersing in the ambient ozone in a sunny day, the NO concentrations are higher than those expected for a non-turbulent chemistry model. The model of Kewley has been questioned by SEINFELD and GEORGOPOULOS [21] because it is based on the assumptions which are inappropriate for the atmospheric conditions. These assumptions are valid for fluid mechanics of combustion devices but not for atmospheric boundary layer.

3.5. A CLASSICAL *K*-THEORY MODEL IN WHICH THE MICRO-MIXING PROCESSES ARE INCORPORATED BY MEANS OF AN "INTERACTION BY EXCHANGE WITH A MEAN MODEL" (I.E.M.)

There are three reactive plume models available in literature in which micro-mixing processes are incorporated by means of an "interaction by exchange with a mean model" (I.E.M). In one of them emissions from an area source are analysed [17]. In two other models, emissions from a point source are considered and these are described in this review [13].

In these reactive plume models, a mean concentration field of chemical species imbedded in a turbulent flow is described by the averaged transport-diffusion chemistry equation. It is closed with respect to the turbulent fluxes with classical *K*-theory. Closure of the mean reaction rate in this equation is achieved by means of the I.E.M. model. In the first reactive plume model, the full, numerical I.E.M. model of VILLERMAUX [17], [46] is used. In the second reactive plume model, the simplified, analytical I.E.M. model is applied.

The averaged transport-diffusion chemistry equation written in Einstein's summation notation has the following form:

$$\frac{\partial \bar{C}_i}{\partial t} + \bar{u}_\alpha \frac{\partial \bar{C}_i}{\partial x_\alpha} = \frac{\partial}{\partial x_\alpha} \left(\bar{u}'_\alpha \bar{C}' \right) + \bar{R}_i, \quad (44)$$

where for any variable $\varphi = \bar{\varphi} + \varphi'$; notation $\bar{\varphi}$ stands for the time average; the prime indicates fluctuation about the average.

As it has been mentioned above for the sake of simplicity, classical K -theory is adopted to close the turbulent fluxes terms. The main attention is focused on the closure of the mean reaction rate.

For the case when two species i and k undergo the bimolecular non-linear reaction according to equation (R1) the chemical term is described by equation (1). The exact calculation of the correlation between the species i and k should be:

$$\overline{C_i C_k} = \iint_{C_i, C_k} C_i C_k P_{\gamma_i \gamma_k}(C_i, C_k) dC_i dC_k, \quad (45)$$

where $P_{\gamma_i \gamma_k}(C_i, C_k)$ is the joint p.d.f. of the species i and k .

Computing the p.d.f. is far from easy. The I.E.M. model is used to derive an approximation of the p.d.f. and to obtain a closed expression of equation (45). The essential advantage gained from the I.E.M. model consists in replacing the joint p.d.f. of two reactive species by the p.d.f. of an inert scalar. The calculation of the correlation $\overline{C_i C_k}$ is then determined at each point of the flow based on the following equation:

$$\overline{C_i C_k} = \int_0^1 C_i^{iem}(\phi) C_k^{iem}(\phi) P_\phi(\phi) d\phi, \quad (46)$$

where $C_i^{iem}(\phi), C_k^{iem}(\phi)$ are the trajectories in the composition space; ϕ is the concentration of inert species defined by the equation:

$$\phi = \frac{\left((C_i - C_k) - (C_i^a - C_k^a) \right)}{\left((C_i^s - C_k^s) - (C_i^a - C_k^a) \right)}, \quad (47)$$

where C_i^s, C_i^a denote the concentrations of the species i at the emission source and in the ambient atmosphere, respectively. The inert species concentration ϕ has the following boundary conditions: $\phi = 0$ in the ambient atmosphere and $\phi = 1$ at the emission source.

The trajectories $C_i^{iem}(\phi), C_k^{iem}(\phi)$ are known after solving a set of I.E.M. equations for reactive species of the system and for the inert species. In the case of the NO-NO₂-O₃ system, in which reactions (R2) and (R3) are taken into account, a set of I.E.M. equations takes the form:

$$\frac{dC_i}{dt} = \frac{\overline{C_i} - C_i}{\tau_m} + R_i \quad \text{for NO, NO}_2, \text{O}_3, \quad (48)$$

$$\frac{d\phi}{dt} = \frac{\overline{\phi} - \phi}{\tau_m} \quad \text{for inert species,} \quad (49)$$

where \bar{C}_i and $\bar{\phi}$ are given after solving the transport–diffusion chemistry equations (44) (including advection and macro-mixing), τ_m is the mixing time related to the turbulent field.

The I.E.M. concept consists in assuming that micro-mixing is achieved by exchanges with the mean environment at a given frequency $1/\tau_m$. The mixing time τ_m in the model of Delamare and co-workers is supplied from the turbulence model of SYKES, LEWELLEN and PARKER [44]. According to this model the dissipation time scale evolves linearly with the dissipation time.

In the full, numerical I.E.M. model, the above set of equations is solved numerically. In the simplified, analytical I.E.M. model, the analytical expressions are derived for $C_i^{iem}(\phi)$ and $C_k^{iem}(\phi)$.

The implementation of I.E.M. within the Eulerian framework is achieved as follows:

1. Solving the averaged Eulerian transport–diffusion chemistry equations (44) provides mean concentration fields. In these equations, turbulent fluxes are closed according to *K*-theory and mean reaction rates are estimated in the framework of the I.E.M. model.

2. Local values of the mixing time τ_m are derived from the turbulence model of SYKES, LEWELLEN and PARKER [44].

3. At each point in the field, the set of equations (48) and (49) is solved using the above local values of \bar{C}_i , τ_m . The mean reaction rate is computed and in turn it is implemented in the Eulerian transport–diffusion chemistry equations in Step 1.

The above procedure is carried out at each time step of the solution algorithm. Of course, mean velocity as well as turbulent diffusivity fields have to be known before solving equations. They may be derived either from a Navier–Stokes calculation and turbulence model, or from surface layer laws [36].

The presented method does not assume the chemical equilibrium and, thereby, is expected to work at any arbitrary Damkoler number. Application of the model to the case of two sources of material, as described, is quite straightforward. However, treating multiple sources requires an extension of I.E.M. that is rather delicate since it is associated with the problem of the distribution of the joint p.d.f. upon multiple trajectories.

The reactive plume models developed by Delamare and co-workers and a model developed by Georgopoulos and Seinfeld (described in section 3.6) were tested on experimental data obtained by BUILTIES [4]. In this experiment, the NO–NO₂–O₃ chemical system was analysed and only one (the most important) reaction (R1) was studied in isolation. The emission of NO from a point source to the ambient O₃ was simulated in a wind tunnel in which neutral atmospheric boundary layer conditions were set down. The models gave good results. The computational time for the analytical reactive plume model of Delamare and co-workers was about ten times shorter than that for the full I.E.M. model. It means that the analytical reactive plume model of Delamare can be applicable to practical computations.

3.6. A MODIFIED *K*-THEORY MODEL IN WHICH MICRO-MIXING PROCESSES ARE INCORPORATED BY MEANS OF THE "CONCENTRATION FIELD SPLITTING APPROACH" (CO-VARIANCES ARE CALCULATED BASED ON THE EXACT ALGEBRAIC RELATION)

A model of GEORGOPOULOS and SEINFELD [21], [22] is based on the transport-diffusion chemical equation for ensemble-averaged concentrations, i.e. mean concentrations refer here to the ensemble averages. It describes pointwise concentration inside instantaneous plumes relative to a centre of mass of each cross-section of meandering plume.

It is assumed that: (i) there is a mean wind along the x_1 -axis; (ii) the molecular diffusion is neglected in the overall process and is incorporated implicitly in the chemical rate that accounts for the effects of fine-scale fluctuations; (iii) turbulent diffusion is neglected in comparison with the mean wind along the x_1 -axis; (iv) the concentration field is in a steady state with respect to the meandering system of co-ordinates; (v) there is no other volume sources/sinks of the species considered except chemical processes.

The transport-diffusion equation is closed with respect to the turbulent term by the first order closure scheme. This scheme is based on the so-called "apparent diffusivity concept" which is the modified *K*-theory concept. It is modified in the sense that *K*-s used are not the properties of the flow field but at any "receptor point" of the specific source receptor pair.

The closure scheme for the chemical term is based on the "concentration field splitting" technique developed by SHU [31], [34]. The parameter called the "relative intensity of plume segregation" allowing measurement of the completeness of the fine-scale mixing is introduced.

Under these conditions the governing equation for the species *i* takes the following form:

$$\bar{u} \frac{\partial \bar{C}_i}{\partial x_1} = \frac{\partial}{\partial y_1} \left(K_y(x_1) \frac{\partial \bar{C}_i}{\partial y_1} \right) + \frac{\partial}{\partial z_1} \left(K_z(x_1) \frac{\partial \bar{C}_i}{\partial z_1} \right) + \bar{R}_i, \quad (50)$$

where \bar{C}_i is the ensemble average concentration of the species *i* at the point (x_1, y_1, z_1) of the meandering co-ordinate system connected to the axis of the instantaneous plume; \bar{u} is the mean wind velocity along the x_1 -axis; K_y, K_z are the horizontal and vertical apparent diffusivity coefficients, respectively; they are determined by the use of relative dispersion parameter δ_{rel} .

In the case of the point release of the species *i* into the uniform field of the species *k* and accepting assumption that the concentrations of the species *i* at least near the plume axis are much greater than the background concentrations of the species *k*, the overall reaction rate \bar{R}_i of reaction:



can be approximated by the following equation:

$$\bar{R}_i = -k_f \bar{C}_i \bar{C}_k + k_f I_i^{in} C_i (\bar{C}_k^{in} - \bar{C}_k) + k_b \bar{C}_p, \quad (51)$$

where C_i^{in} , C_k^{in} are the ensemble average concentrations of inert surrogate species; k_f , k_b are the forward and backward rate coefficients of reaction (R6); I_i^{in} is the relative intensity of segregation fluctuation of the inert species i given by:

$$I_i^{in} = \frac{\overline{(C_i^{in})'^2}}{C_i^{in2}}. \quad (52)$$

In case when the number of independent reactions is smaller than the number of reacting species, the so-called "reaction progress variable" is introduced in order to simplify the complexity of description of this chemical system. The progress variable is defined by the following relation:

$$\zeta(x_1, y_1, z_1, t) = \frac{C_i(x_1, y_1, z_1, t) - C_i^{in}(x_1, y_1, z_1, t)}{\nu_i}, \quad (53)$$

where ν_i is the stoichiometric coefficient of the species i ; C_i , C_i^{in} are the concentrations of the species i and its inert surrogate species in the meandering co-ordinate system, respectively.

The governing equation (equation (50)) with respect to the progress variable takes the following form:

$$\bar{u} \frac{\partial \bar{\zeta}}{\partial x_1} - K_y(x_1) \frac{\partial^2 \bar{\zeta}}{\partial y_1^2} - K_z(x_1) \frac{\partial^2 \bar{\zeta}}{\partial z_1^2} = \bar{R}_i, \quad (54)$$

where $\bar{\zeta}$ is the reaction progress variable at the point (x_1, y_1, z_1) of the meandering co-ordinate system; K_y , K_z are the horizontal and vertical apparent diffusivity coefficients, respectively; \bar{u} is the mean wind velocity along the x_1 -axis.

The overall mean rate of the reaction \bar{R}_i is approximated by the quadratic expression in $\bar{\zeta}$, in which coefficients are functions of properties of inert surrogate fields, i.e. functions of \bar{C}_i^{in} , \bar{C}_k^{in} , \bar{C}_p^{in} as well as of chemical coefficients k_f , k_b .

Once the governing equations of the evolution of $\bar{\zeta}(x_1, y_1, z_1, t)$ as well as of the inert surrogate mean concentration fields $\bar{C}_i^{in}(x_1, y_1, z_1, t)$ have been formulated and solved, the mean concentration of any reacting species is directly calculated:

$$\overline{C_i(x_1, y_1, z_1, t)} = \overline{C_i^{in}(x_1, y_1, z_1, t)} + v_i \overline{\zeta(x_1, y_1, z_1, t)}. \quad (55)$$

The model of Georgopoulos and Seinfeld was tested on the experimental data of BULTJES [4] for the NO-NO₂-O₃ system. In this experiment, the emission of NO from a point source to the ambient O₃ was simulated in a wind tunnel in which neutral atmospheric boundary layer conditions were set. In the calculations, assumptions allowing simplification of computational procedure were accepted. These assumptions are as follows: (i) the Gaussian formula is used to calculate the concentrations of inert species; (ii) the dispersion parameter δ_{rel} is estimated based on the semi-empirical formula; (iii) the intensity of plume segregation is determined with the "localised production of fluctuations model" (L.P.F.M.).

The model of Georgopoulos and Seinfeld is capable of predicting quantitatively the retardation of the evolution of non-linear plume chemistry caused by incomplete mixing. The calculations show that if we neglect turbulent fluctuations of concentrations in the NO-NO₂-O₃ system we will deal with inaccuracies in a simulation of plume chemistry close to a source, but if we use an appropriate instantaneous plume width, the degree of conversion sufficient for downwind is correctly computed. For this reason we suggest that it is not critical to incorporate treatment of turbulent chemistry in the current models as long as the treatment of a basic plume entrainment processes in the models are adequate [21], [22].

3.7. PROBABILITY DENSITY FUNCTION (P.D.F.) MODELS

There is one model of this type dealing with the atmospheric problems found in the literature. It is described in the paper of GONZALES [24]. This model was applied to study reactive plume emitted from an area source and from a point source. This review concerns reactive plume models of point sources, that is why only the application of the model of Gonzales to a point source is discussed.

The p.d.f. models are based on the p.d.f. transport equation. The method works at the arbitrary Damkoler number and naturally includes macro-mixing through mean advection and turbulent diffusion. The p.d.f. equation has a closed reactive term and thereby includes exactly the effect of turbulence fluctuations of concentrations on chemical reactions.

The usability of the p.d.f. approach appears to diminish when solutions of the p.d.f. transport equations are considered. Analytical solutions of the p.d.f. transport equations have been obtained in a few simple cases. To solve those equations in a general case numerical methods are required. In such methods, the integro-differential nature of equations and their complexity have to be taken into account. Reactive flows of practical interest usually involves many species and consequently dimensionality of the p.d.f. is large. An order-of-magnitude analysis shows that a finite-difference solution of the p.d.f. transport equation is impracticable for a number of species greater than 3. In addition, the computational expense is found to rise exponentially with dimensionality of p.d.f. A Monte Carlo method is devised to simulate

a finite-difference solution of the p.d.f. transport equation. The computational expense of the Monte Carlo method rises only linearly with dimensionality of p.d.f. and it is the best that can be achieved by any algorithm.

Assuming that: (i) there is the constant density; (ii) molecular diffusivities are equal; (iii) the Peclet number is large, the equation for the joint p.d.f. of the species 1, 2, ..., N written in Einstein's summation notation takes the following form:

$$\begin{aligned} & \frac{\partial p}{\partial t} + \bar{u}_\alpha \frac{\partial p}{\partial x_\alpha} - \frac{\partial}{\partial \psi_i} (R_i(\psi_1, \psi_2, \dots, \psi_N) p) \\ &= - \frac{\partial}{\partial x_\alpha} \left(\overline{(u'_\alpha | C = \Psi)} p \right) - \frac{\partial^2}{\partial \psi_i \psi_k} \left(\overline{(\varepsilon_{i,k} | C = \Psi)} p \right), \end{aligned} \quad (56)$$

where $p(\psi_1, \dots, \psi_N; x, t)$ or p for the sake of simplicity is the one-point joint p.d.f. of the species 1, ..., N ; ψ_i is the sample space variable corresponding to the concentration C_i for any variable ϕ : $\phi = \{u_\alpha, \varepsilon_{i,k}\}$; $\bar{\phi}$ is the mean value of ϕ , and ϕ' is its fluctuation around the mean; $\overline{\phi | C = \Psi}$ is the conditional mean of ϕ given by $C = \Psi$; $R_i(\psi_1, \psi_2, \dots, \psi_N)$ is the chemical reaction rate of the species i ; $\varepsilon_{i,k}$ represents the components of the scalar dissipation rate tensor given by:

$$\varepsilon_{i,k} = D \frac{\partial C'_i}{\partial x_\alpha} \frac{\partial C'_k}{\partial x_\alpha}, \quad (57)$$

where D is the molecular diffusivity of the species i ; $D_i = D$ for all species.

The terms on the right-hand side of equation (56) are not closed. The first one, i.e. the conditional convection, is the counterpart of turbulent transport of concentration moments $\overline{u'_\alpha C'_i}$. The second one is the conditional scalar dissipation and represents the counterpart of the dissipation of concentration variance and higher-order concentration moments.

The convective term is usually closed owing to a conventional gradient transport model [35]:

$$\overline{(u'_\alpha | C = \Psi)} p = -K_\alpha \frac{\partial p}{\partial x_\alpha}, \quad (58)$$

where K_α is the eddy diffusivity tensor.

Closure of the dissipation term still promotes intensive research activity [15]. A simple model is the linear mean square estimation (L.S.M.E.) model [35] following the concept:

$$- \frac{\partial^2}{\partial \psi_i \psi_k} \left(\overline{(\varepsilon_{i,k} | C = \Psi)} p \right) = \frac{1}{\tau_m} \frac{\partial}{\partial \psi_i} \left((\psi_i - \bar{C}_i) p \right), \quad (59)$$

where τ_m is the characteristic scalar micro-scale.

From equations (56)–(59) the modelled equations for the joint p.d.f. of reactive species transported in a turbulent flow is:

$$\begin{aligned} \frac{\partial p}{\partial t} + \bar{u}_\alpha \frac{\partial p}{\partial x_\alpha} - \frac{\partial}{\partial \psi_i} (R_i(\psi_1, \psi_2, \dots, \psi_N)p) \\ = \frac{\partial}{\partial x_\alpha} \left(-K_\alpha \frac{\partial p}{\partial x_\alpha} \right) + \frac{1}{\tau_m} \frac{\partial}{\partial \psi_i} ((\psi_i - \bar{C}_i)p). \end{aligned} \quad (60)$$

Solving equation (60) requires that the flow transport variables \bar{u}_α and K_α as well as τ_m are supplied. These parameters can be achieved either from the given law or from the Navier–Stokes computation and turbulence modelling.

The principle of the Monte Carlo simulation is the following [38]:

1. At each node of a computational mesh the p.d.f. $p(\psi_1, \dots, \psi_N)$ is represented by the ensemble of N_p representative values or, in another words, each concentration C_i (corresponding to the species i) assumes N_p random values, say $C_i^{(1)}, \dots, C_i^{(N_p)}$, $i = 1, \dots, N$. This gives a set of $N \times N_p$ values at each point. These ensembles are modified at each time step so as to simulate each of four processes: diffusion, convection, reaction and mixing.

2. In each direction x_α , convection is simulated by selecting at random at each node, $c_\alpha N_p$ elements and replacing them by elements selected at random from the upstream node. The variable c_α is the local Courant number: $c_\alpha = |\bar{u}_\alpha| \Delta t / \Delta x_\alpha$, where \bar{u}_α is the local mean velocity, Δt is the time step and Δx_α the local node-spacing.

3. Once all ensembles have been modified by convection, the diffusion process is applied. It is simulated in the following way: at each node along the direction x_α the elements $\gamma_\alpha^- N_p$ and $\gamma_\alpha^+ N_p$ are selected at random from the ensemble elements N_p .

Then the group of the elements $\gamma_\alpha^+ N_p$ is exchanged with the group of the elements $\gamma_\alpha^- N_p$ of the next node on the line. The terms γ_α^- and γ_α^+ are the local Fourier numbers: $\gamma_\alpha^- = K_\alpha (x_\alpha - 0.5x_\alpha) \Delta t / \Delta x_\alpha^2$, where K_α is the eddy diffusivity tensor. For convection and diffusion each direction is considered in turn. POPE [38] has demonstrated that the solution of the above simulation fully approximates the solution of the fully explicit finite-difference scheme that will be accurate to the first order for convection and the second order for diffusion.

4. Chemical reaction is implemented considering that at each node, the elements N_p react for a time interval Δt according to a set of differential equations:

$$\frac{dC_i^{(n)}}{dt} = R_i(C_1^{(n)}, \dots, C_N^{(n)}) \quad \text{for } i = 1, \dots, N \text{ and } n=1, \dots, N_p. \quad (61)$$

5. Finally the L.M.S.E. model implies that micro-mixing modifies the composition of the elements during the time interval Δt :

$$\frac{dC_i^{(n)}}{dt} = \frac{\overline{C_i} - C_i^{(n)}}{\tau_m} \quad \text{for } i = 1, \dots, N \text{ and } n = 1, \dots, N_p. \quad (62)$$

The complete procedure, i.e., convection, diffusion, reaction and mixing, is applied at each time step and at all nodes of the computational domain until stationary state is reached.

Statistical quantities at each point (mean values, variances, co-variances) are simply derived by performing ensemble average operations. The ensemble average of any function $\lambda(C_1, \dots, C_N)$ is:

$$\langle \lambda(C_1, \dots, C_N) \rangle = \frac{1}{N_p} \sum_{n=1}^{N_p} \lambda(C_1^{(n)}, \dots, C_N^{(n)}). \quad (63)$$

The p.d.f. model of Gonzales was used to have further insight into the effect of microscale turbulence on chemical reactions. In the test, the experimental data obtained by BUILTIES [4] were applied. In the experiment, the NO-NO₂-O₃ chemical system was analysed. It was assumed that: (i) NO was supplied from the point source; (ii) we dealt with neutral atmospheric conditions and constant wind velocity; (iii) the mean concentration of background ozone was maintained constant, (iv) only forward chemical reaction given by (R1) occurred. It was justified as the experiment was undertaken without light irradiance.

In the framework of the study of Gonzales, τ_m was assumed to be the same for the inert and reactive species and was evaluated following a turbulent transport model of SYKES [44]. The values of eddy diffusivities K were derived from the plume dispersion parameters δ_y and δ_z . The comparison of predictions with experimental data shows that the method is reliable for addressing environmental problems. A satisfactory agreement was found.

3.8. LARGE EDDY SIMULATION (L.E.S) MODELS OF REACTING PLUME

L.E.S. is a numerical technique in which large-scale, energy containing eddies are resolved explicitly and only small-scale, sub-grid motions are parametrized.

Two numerical reactive plume models, which fall into this class, are found in the literature. These are: a model of SYKES and co-workers [45] dealing with emission from a single point source and a model of SCHUMANN and co-workers dealing with emission from an area source plume [39], [40]. Because this review is devoted to reactive plume models for point sources, here the model of Sykes and co-workers is described.

In the model of Sykes and co-workers, the set of equations to be solved is as follows: the filtered equations of motion together with a sub-grid stress model and the filtered transport-diffusion chemistry equation. By "filtering" we mean here the elimination of the small-scale motions that are smaller than the numerical grid. The

filter conservative equation for the species i written in Einstein's summation notation is as follows [45]:

$$\frac{\partial \hat{C}_i}{\partial t} + \frac{\partial (\hat{u}_\alpha \hat{C}_i)}{\partial x_\alpha} = \frac{\partial}{\partial x_\alpha} \left(K_{SG} \frac{\partial \hat{C}_i}{\partial x_\alpha} \right) - k_r \hat{C}_i C_k + \hat{S}_i(x_\alpha) \quad (64)$$

where for any variable φ : $\varphi = \{C_i, u_\alpha, s_i\}$, $\hat{\varphi}$ and φ_{SG} denote the filtered value of φ and its deviation from the mean, respectively; \hat{u}_α is the velocity, \hat{C}_i is the instantaneous concentration of the species i ; K_{SG} is the sub-grid eddy diffusivity obtained from L.E.S; \hat{S}_i is the source term for the species i .

In equation (64), the sub-grid fluctuations of concentrations are ignored, i.e. $\hat{C}_i \hat{C}_k = \hat{C}_i \hat{C}_k + C_{i,SG} C_{k,SG} \cong \hat{C}_i \hat{C}_k$. This is done based on the results of non-reactive plume simulations, which indicate that sub-grid fluctuations of concentrations are small in comparison to the resolved part of the total variance. However the authors emphasize that the effects of sub-grid fluctuations on chemical reactions are not well known and need further study.

In the model of Sykes and co-workers, an idealised simple NO-NO₂-O₃ chemical system, in which only one reaction (R1) is taken into account, is analysed. The reverse reaction, which is principally photochemical, is ignored. Analysis of this key reaction in isolation was chosen for the purpose of simplifying the system.

The model of Sykes and co-workers was used to investigate the influence of turbulence on non-linear chemical reactions. The numerical results were obtained under the following conditions: (i) a 48×48×60 grid in a domain of 2.67L×1.33L×4.6L in the (x,y,z) directions, respectively, where L is the boundary layer height; (ii) a uniform ambient ozone concentration, typical of the atmospheric boundary layer; (iii) a non-buoyant and momentum-less source containing both ambient ozone and a specified concentration of NO; (iv) the source specified as a spherical volume with a diameter of 0.0292 L.

The simulations give the 4-dimensional, in space and time, development of the concentration field. They were run for a total time of 4250 sec in a 20 km long domain. In order to get a reliable statistics, eight realisations were obtained for each source condition by moving the source to a different horizontal location flow. Effects of different reaction rates were investigated by varying the source NO concentration, while maintaining a constant ambient ozone level.

The simulations demonstrate that the rate of NO₂ production is significantly affected by the turbulent nature of the dispersing plume. The effect of an incomplete turbulent mixing of the two reactants on the reaction rate can persist for long downstream distances, particularly for the high NO levels typical of power plant stacks. The L.E.S results also show that the important measure of turbulent fluctuations, the turbulence segregation coefficient I_s , may be reasonably approximated by a constant value over most of plume cross-section.

An appropriate implementation of L.E.S in the reactive case raises the problem of modelling sub-grid chemical terms, which is still a challenging task.

4. CONCLUSIONS AND REMARKS

Based on this two-part review of chemically reactive plume models the following conclusions and remarks can be formulated:

1. There is a large variety of chemically reactive plume models. They differ in the description of turbulent mixing processes and in the complexity of the chemical schemes applied. Typically, the more complex description of turbulent mixing processes in the model, the more simple chemical system.

2. Chemically reactive plume models incorporating macro-mixing processes, described in part I of this review, have been an important aid of learning about the influence of environmental parameters on the plume dispersion. These models are a useful tool in engineering studies.

3. Chemically reactive plume models incorporating macro- and micro-mixing processes, described in part II of this review, are an excellent investigation tool in scientific studies. They allow us to have a further insight into the effect of micro-scale turbulence on chemical reactions.

4. Modelling of chemically reactive flows is a developing discipline. Development of knowledge in this field and a better understanding of the behaviour of chemically reactive species in the atmospheric boundary layer as well as new modelling techniques allow us to improve the existing models and to develop more advanced models.

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PRZEGLĄD MODELI SMUG REAKTYWNYCH CHEMICZNIE) CZĘŚĆ II. MODELE UWZGLĘDNIAJĄCE PROCESY MAKRO- I MIKROMIESZANIA

Przedstawiono modele smug reaktywnych chemicznie. Opisują one proces powstawania zanieczyszczeń wtórnych w smugach emitowanych z wysokich punktowych źródeł emisji. Modele zostały podzielone na klasy zależnie od sposobu, w jaki opisano procesy turbulencyjnego mieszania. Termin *mieszanie turbulencyjne* obejmuje makromieszanie i mikromieszanie. *Procesy makromieszania* odnoszą się do zmian stężeń średnich, podczas gdy *procesy mikromieszania* są związane z fluktuacjami stężeń, tj. z odchyleniami stężeń od wartości średnich. Przedstawiono modele dotyczące procesów mikromieszania oraz modele opisujące zarówno mikro-, jak i makromieszanie. Łącznie wyróżniono 8 grup modeli. Dla każdej z grup omówiono główne założenia i podstawowe równania matematyczne. Podano wyniki testowania i przykłady zastosowania modeli.

modele smug
smugi...
zanieczyszczenia wtórne