FLUXES AND (CO-)VARIANCES OF REACTING SCALARS IN THE CONVECTIVE BOUNDARY LAYER

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1. INTRODUCTION

The chemical lifetime of reactants in the atmosphere can vary from some minutes to days. For reactants with a short chemical lifetime or with a lifetime at the same order of magnitude as the turnover time of the convective boundary layer (CBL), the turbulent mixing limits the chemical transformations (Vilà-Guerau de Arellano and Lelieveld, 1998). This process therefore influences the distribution of reacting scalars and the chemical composition of the CBL, and in particular the second-order moments, i.e. fluxes and (co-)variances. By including the chemical terms in the governing equations for reactants, one can study the relevance of the chemistry on the fluxes and (co-)variances. For similar timescale of turbulence and chemistry, one should expect that the chemical terms might have a contribution similar to the one of dynamical terms and, as a result, fluxes and (co-)variances deviate from the inert profiles. We are analyzing the magnitude of these deviations as these quantities, which describe the transport, the variability and the mixing of reacting scalars, are relevant for atmospheric chemistry.

Compared to temperature, moisture and inert scalars for which extensive studies have shown the contribution of the different dynamical terms to the budget of fluxes and (co-)variances (Wyngaard *et al.*, 1978; Lenschow *et al.*, 1980; Moeng and Wyngaard, 1984; 1989), only few studies have been partially addressed to reacting scalar second-order moment budgets. For instance, investigations on the contribution of third-order moments to the chemical term of reacting scalar flux budget equation have been performed using a reduced chemical mechanism and a second-order reaction (Petersen, 2000). However, a comprehensive study of the effect of the chemical term on the flux and (co-)variance is still lacking. In this study, the effect of the chemical term on the transport and mixing of reacting scalars is analyzed by carrying out the exact decomposition of second-order moment budgets by means of large-eddy simulation (LES). Moreover, a parameterization of the effect of uncomplete mixing on chemical transformations is developed. The simulations are involving a bottom-up diffusive species (A) injected at the surface and a top-down one (B) which is entrained at the top of the CBL. As chemical cases, we have simulated representative turbulent reacting flows in a CBL with a second-order irreversible reaction and a chemical mechanism in equilibrium.

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2. NUMERICAL SETUP

We simulate an entraining CBL with a surface sensible heat flux of $0.052 \ Kms^{-1}$ and no latent heat flux. The geostrophic wind is chosen equal to zero and the initial potential temperature profile has a constant value of $288 \ K$ below 662.5 meters and is increasing by $0.6 \ K$ each hundred meters above 712.5 meters. The grid prescribed has 64 x 64 x 60 points in the horizontal and vertical directions, it represents a domain of $3.2 \ km$ x $3.2 \ km$ x $1.5 \ km$. Periodic lateral boundary conditions are assumed. The maximum time step used in the calculation is $0.5 \ s$. The simulation covers a 2 hours period and the statistics presented here are obtained averaging the results over the last hour of calculation. For all the simulations, the convective velocity scale w_*, the CBL height z_i and the free convection timescale $t_* \equiv z_i/w_*$ are respectively equal to $1.096 \ ms^{-1}$, $747 \ m$ and $680 \ s$.

Previous research (Schuman, 1989; Sykes *et al.*, 1994 and Vilà-Guerau de Arellano and Lelieveld, 1998) have defined a reacting flow classification based on the Damköhler number Da_i for a reactant i. For the CBL, this number is defined as $\frac{z_i}{w_*}k\langle C\rangle$ where $\langle C\rangle$ accounts for the bulk concentration of reacting scalar C. Using this classification, we have performed four numerical experimentations: inert (I), moderately slow (MS), moderately fast (MF) and cycle (C). The simulations are involving a bottom-up diffusive species (A) injected at the surface, with a surface flux of $0.1 \ ppbs^{-1}$ and a top-down one (B) entrained at the top of the CBL. The different chemical cases are defined using reactions 1 and 2.

$$A \ + \ B \ \xrightarrow{k} \ C, \tag{1}$$

$$C \ \xrightarrow{j} \ A \ + \ B. \tag{2}$$
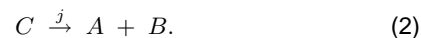
In the MS and MF experiments, the scalars A and B solely undergo the reaction (1), i.e. the photolytic rate constant j is set at 0. The reaction rate k value has be chosen in order to give appropriate Damköhler numbers related to the emitted scalar i.e. $Da_A = 0.6$ for the MS chemistry and $Da_A = 4.1$ for the MF one. For MS, the initial B concentration profile has a constant value of $0.5 \ ppb$ below 662.5 meters and $2 \ ppb$ above this level, for MF the values are respectively equal to $1 \ ppb$ and $10 \ ppb$. In addition, a cycle (chemical case C) composed of reactions (1) and (2) is also discussed to determine the role of chemical equilibrium in the second-order moments. Indeed, the control parameter of a reacting scalar undergoing a chemical cycle is not equal to the individual Damköhler numbers defined previously but to an overall

Da (Krol *et al.*, 2000) defined as the sum of individual Da_i weighted by the stoichiometric coefficient as it appears in the conservation equation for reacting scalars, e.g. $|Da_A - Da_C \frac{\langle C \rangle}{\langle A \rangle}|$ for reactant A. Reaction (2) is photolyzed at a reaction rate constant $j = 100k$ assuming that photolytic reactions are faster than the second-order ones.

3. REACTING FLUXES

Figure 1 shows the vertical profiles of scalar fluxes which consist of a resolved part and a sub-grid scale contribution modelled as a diffusion process. Within the boundary layer, the inert scalars profiles (temperature and bottom-up scalar for the inert chemical case) are following a linear shape (Deardorff, 1979; Wyngaard and Brost, 1984). For reactive scalars, the profiles deviate from this shape. These deviations become more significative when the Damköhler number is increasing, e.g. MS show little deviations whereas the deviations are important for MF. This has been already noticed by Gao and Wesely (1994) and Sykes *et al.* (1994). These deviations are due to the effect of chemistry which acts as a sink term in the flux budget. As the chemical contribution to fluxes is increasing with the reaction rate, the deviations will increase with the reaction rate and in consequence with the Damköhler numbers. In the cycle case, the system is reaching a chemical equilibrium where the destruction of a chemical species by one reaction is balanced by the chemical production by the other one. In other words, the chemical term in the flux budget equation is composed of a sink and a source term.
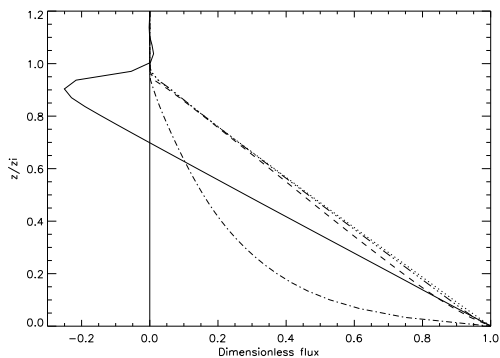

FIG. 1: Vertical profiles of the dimensionless fluxes for the bottom-up scalars. The heat flux is represented by a solid line. The chemical fluxes for the different chemical cases are presented: Inert (dotted line), MS (dashed line), MF (dash dot line) and C experiments (dash dot dot dot line). The values are made dimensionless by $w_*\theta_*$ for the temperature and w_*c_{u*} for the chemical fluxes where θ_* and c_{u*} are respectively the temperature scale and the chemical scale defined as the ratio of the surface flux by the convection velocity scale.

The Damköhler numbers are used to classify the reacting flows with respect to the governing equation for scalar. It is convenient to introduce dimensionless numbers accounting for the chemical contribution to

fluxes. Writing the flux budget equation in a dimensionless way and assuming that chemical third-order moment can be neglected (Petersen, 2000), one can define flux Damköhler numbers as:

$$Da_{\overline{wa}} = \left| Da_A + Da_B \frac{w_*b_*}{w_*a_*} - Da_C \frac{w_*c_*}{w_*a_*} \right|, \quad (3)$$

where Da_A, Da_B and Da_C are respectively the Damköhler numbers for the species A, B and C with respect to the second-order reaction (1) for A and B and to the photolytic one (2) for C. a_*, b_* and c_* are the concentration scales as defined in Cuijpers and Holtslag (1998). The value of this number show the relevance of accounting for chemistry in flux budget equation. C experiment results on figure 1 (e.g. no relevant deviation from inert shape) and on table 1 ($Da_{\overline{wa}} = 0.4$) show that the flux Damköhler numbers is an appropriate control parameter for estimating the chemical impact on vertical reactant profiles.

	MS	MF	C
Da_A	0.6	4.1	6.2
$Da_{\overline{wa}}$	0.5	3.9	0.4
$Da_{\overline{ab}}$	3.3	2.2	0.8

Table 1: First and second-order Damköhler numbers. $Da_{\overline{ab}}$ are determined using a similar expression to eq. 3.

4. REACTING COVARIANCES

The chemical transformations in the CBL depends on the efficiency of reactant mixing. This efficiency is determined by the ability of turbulence to bring the reactants together. In the case of non-premixed reacting scalars, the reaction rate can be slow down due to heterogeneous mixing. The covariance between reactants, i.e. $\overline{ab}$, is the variable which accounts for the segregation of species in the CBL. It is an explicit term in the averaged governing equation for the concentration.

Figure 2 shows the vertical profiles of the resolved concentration fluctuation covariances. As for the fluxes, the impact of chemical term is increasing for higher reaction rates. For MS and MF experiments, the profiles deviate significantly for the inert shape. For the moderately fast chemical case, these deviations are more significative in the upper-CBL. The MS covariance profile is affected in the major part of the CBL. This latter is the most affected by chemistry ($Da_{\overline{ab}} = 3.3$). As shown by the covariance Damköhler number for C experiment ($Da_{\overline{ab}} < 1$), the vertical profile for reactants undergoing a chemical cycle is rather similar to the one of inert scalars.

A chemical term has been introduced in the budget equations in order to study the chemical contribution to covariance (eq 4).
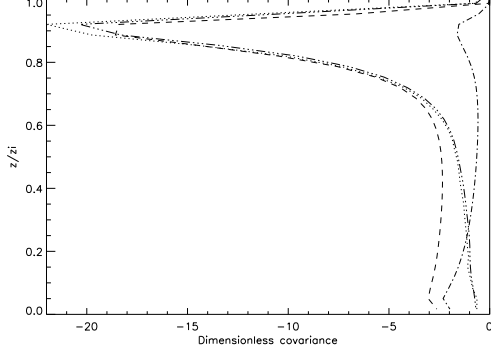
FIG. 2: Vertical profiles of dimensionless reacting scalar covariances. The different chemical cases are plotted: Inert (dotted line), MS (dashed line), MF (dash dot line) and C experiments (dash dot dot dot line). The values are made dimensionless by $c_{u*}c_{d*}$. The top-down chemical scale, c_{d*}, has been calculated by taking the absolute value of the ratio of the top-down inert scalar flux at z_i by the convective velocity scale w_*.
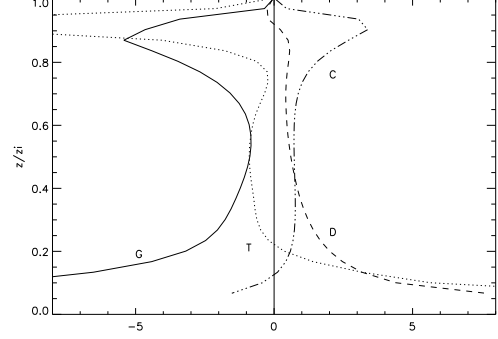

FIG. 3: Dimensionless budget of the resolvable-scale scalars covariance for the MF experiment. The gradient (G) term, the turbulent transport (T) and the dissipation at smaller scales term (D) are respectively represented using solid, dotted and dashed lines. The chemical term (C) is plotted in dash dot dot dot lines.

$$\frac{\partial \overline{ab}}{\partial t} = -\underbrace{\overline{wa}\frac{\partial B}{\partial z} - \overline{wb}\frac{\partial A}{\partial z}}_{G} - \underbrace{\frac{\partial \overline{wab}}{\partial z}}_{T}$$
$$-\underbrace{a\frac{\partial \langle b''u_k''\rangle}{\partial x_k} - b\frac{\partial \langle a''u_k''\rangle}{\partial x_k}}_{D} + \underbrace{R_{\overline{ab}}}_{C}, \quad (4)$$

where the terms on the right hand side are respectively the gradient term (G), the turbulent transport (T) contributions, the dissipation at the subgrid scale (D) and the chemical contribution (C). For MS and MF, this latter reads

$$R_{\overline{ab}} = -k\left(\overline{ab}B + \overline{ab}A + \overline{a^2}B + \overline{b^2}A + \overline{a^2b} + \overline{b^2a}\right). \quad (5)$$

Figure 3 shows the budget of the resolvable-scale scalars covariance for the MF experiment. All the different contributions have the same order of magnitude in the mid-CBL. The chemical term acts as source in the main part of the CBL and as sink near the surface. The chemical term in the budget equation (see eq. 5) is composed by different contributions with opposite impacts on covariance behavior. As the scalar are always anti-correlated in our experiments, the terms related to the product of the covariance to the mean scalar concentration (i.e. $-k\overline{ab}B$ and $-k\overline{ab}A$) acts as sources. The variance containing terms, $-k\overline{a^2}B$ and $-k\overline{b^2}A$, are always a sink as the scalar variances are positive. If the term 5 acts as a total sink or source depends on the order of magnitude of the single variance/covariance contributions.

5. PARAMETERIZATION OF THE REACTANT SEGRE-GATION

We have shown previously that the chemical contribution to covariance has an important impact of their pro-

files if $Da_{\overline{ab}} \simeq 1$ and chemistry is out of balance. In this last section, we derive a parameterization to account for the segregation of species in a CBL. In the derivation we use of the LES results to evaluate the parameterization.

A proper number to characterize the state of mixing of reactant in the CBL is the vertical profile of the intensity of segregation (I_s) defined as the ratio of the fluctuation reactant concentration covariance by the product of the mean concentration:

$$I_s = \frac{\overline{ab}}{AB}. \quad (6)$$

As the concentration fluctuation covariance is the variable which accounts for the segregation of species, it constitutes the starting point of our derivation. This covariance is related to the correlation coefficient ρ following:

$$\rho = \frac{\overline{ab}}{\sigma_A \sigma_B}, \quad (7)$$

where σ_A and σ_B are the standard deviations of the reactants.

In our LES results, we found that ρ has an almost constant value in the whole CBL for the moderately slow and fast chemistry (between -0.6 and -0.8 in both cases). In case of chemical equilibrium or no chemistry, its value is varying from -0.4 at the bottom of the CBL bulk to -0.9 at the top. Averaging the correlation coefficient over the entire CBL gives $\langle\rho\rangle = -0.75$ where the brackets represent the average over the whole CBL. Measurements from aircrafts (Vilà-Guerau de Arellano *et al.*,1993) gave a averaged value around -0.7. Assuming this constant value with depth $\langle\rho\rangle = -0.75$ and combining eq. 6 and eq. 7, we can write

$$I_s = \langle\rho\rangle\frac{\sigma_A \sigma_B}{AB}, \quad (8)$$

where A and B are the concentration profiles with its respective vertical profiles standard deviation σ_A and σ_B.

Figure 4 shows a comparison between I_s calculated using eq. 8 (e.g. with standard deviations and concentrations determined by LES) and I_s determined by LES where reactant covariances are explicitly calculated e.g. using eq. 6. The values of I_s obtained with LES and with the proposed parameterization are in close agreement. Currently we are deriving a more complete expression of eq. 8 where σ_A and σ_B are calculated from (co-)variances functions as defined by Moeng and Wyngaard (1984) including a correction for chemistry.
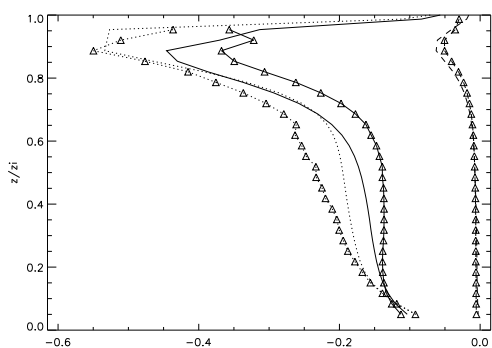

FIG. 4: Intensity of segregation profiles calculated by LES (thick lines) and using a correlation coefficient equal to -0.75 (lines with triangles). The solid lines are used for the MS experiment results, the dotted and dashed ones illustrates respectively the MF and C experiments.

6. CONCLUSION

The effect of chemistry on second-order moments of reactants is studied by means of large eddy simulation. Four chemical cases representative of different reacting flows and involving bottom-up and top-down reactants are simulated. The relevance of the chemical contribution to second-order moments is investigated calculating chemical terms in their budget equations. A detailed analysis of flux and covariance budgets is carried out and the contribution of chemical term is discussed with respect to fluxes and covariances Damköhler numbers.

The results showed that chemical contribution affects strongly reactant fluxes and (co-)variances. By increasing the reaction rate, the deviations of second-order moment profiles from the inert shape are larger. For fluxes, chemistry acts as a sink for both scalars. For covariance, the chemical contribution can be acting as a source or a sink depending on the reaction rate. When the chemistry is in equilibrium, the chemical term becomes negligible and therefore the flux and (co-)variance profiles are similar to the ones of inert scalars.

An expression of the intensity of segregation to be included in larger scale models is proposed by introducing the correlation coefficient ρ between the two reactants. Using the constant value with depth $\langle \rho \rangle = -0.75$ calculated from LES results, it shows I_s profiles in good agreement with LES-calculated ones.

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