

## A dynamic similarity subgrid model for chemical transformations in large-eddy simulation of the atmospheric boundary layer

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[1] In large-eddy simulations (LESs) of atmospheric reacting flows, homogeneous and instantaneous mixing of reactants within a grid-cell is usually assumed. However, highly reactive species are often segregated or pre-mixed at small scales. In this paper, we propose a parameterization to account for the effect of the unresolved scales on the chemical transformations. Its formulation relies on the description of the subgrid unresolved reactant covariance as a function of the resolved covariance by using scale-similarity arguments. A dynamic procedure is used to compute the model coefficient from the resolved reactant concentration fields, therefore not requiring any parameter specification or tuning. In simulations of a convective boundary layer with a fast second-order reaction, using the new model is found to perform better than ignoring subgrid chemistry effects. **Citation:** Vinuesa, J.-F., and F. Porté-Agel (2005), A dynamic similarity subgrid model for chemical transformations in large-eddy simulation of the atmospheric boundary layer, *Geophys. Res. Lett.*, 32, L03814, doi:10.1029/2004GL021349.

### 1. Introduction

[2] Atmospheric boundary layer (ABL) processes, and in particular turbulence, affect the concentration and the reaction rate of trace gases such as ozone, nitrogen oxides and volatile organic compounds [Kley, 1997]. Turbulent eddy motions (e.g., thermals and subsidence motions typical of convective conditions) are responsible for the transport and mixing of reacting species. These processes affect the local interactions between reactants and, consequently, the overall reaction rates and reactant concentrations. This effect of the turbulence on the chemistry is highly dependent on the ratio between the time scales associated with the chemical transformations and the characteristic time scales of the turbulent eddies.

[3] Large-eddy simulation (LES) is becoming an important tool for studying turbulent transport and mixing of reacting chemical species in the ABL. The scales associated with turbulent motions in the boundary layer range from the Kolmogorov dissipation scale (on the order of a millimeter) to the boundary layer depth (on the order of a kilometer). The largest eddies are responsible for the turbulent transport of scalars and momentum whereas the smallest ones are mainly dissipative. LES consists of explicitly resolving all scales of turbulent transport larger than the grid scale (on the order of tens of meters in the

ABL), while the smallest (less energetic) scales are parameterized using a subgrid-scale (SGS) model. For a review of the LES technique and subgrid-scale modeling, see Pope [2000], Meneveau and Katz [2000] and Sagaut [2002].

[4] The chemical lifetime of reacting chemical compounds varies over a wide range of scales. The so-called long lived species are transported and well mixed throughout the boundary layer. More reactive compounds are affected by the turbulent structure of the ABL leading to a non-uniform distribution. For reactants with a short chemical lifetime (shorter than the turnover time of the convective boundary layer, approximately 10–20 minutes) the chemical transformations can be limited by the turbulent mixing. Numerical studies of the effect of turbulence on chemistry in the ABL using LES have been mostly restricted to moderately fast reacting flows involving a second-order reaction between a pollutant emitted at the surface and one entrained from the free troposphere [Schumann, 1989; Sykes *et al.*, 1994; Molemaker and Vilà-Guerau de Arellano, 1998; Petersen, 2000; Vinuesa and Vilà-Guerau de Arellano, 2003]. In these studies, it is assumed that chemical species are perfectly mixed at scales smaller than the LES filter scale. Such an assumption is only justified when the chemistry is slow with respect to the subgrid mixing. This condition may not always be satisfied, especially for highly reactive compounds such as  $OH$  or  $HO_2$ . For instance, Krol *et al.* [2000] reported that common reactions such as  $OH$  with  $RH$  or  $OH$  with  $NO_2$  can be classified within the fast chemical regime. Moreover, Meeder and Nieuwstadt [2000] reported the importance of the subgrid scale mixing of the reactants on the reaction rate in LES. Therefore, large-eddy simulations with realistic atmospheric chemical schemes may require a SGS model for the subgrid reactant covariance, i.e., the quantity that accounts for the mixing at subgrid scales.

[5] Subgrid chemistry effects have typically been neglected in LES of atmospheric turbulent flows [e.g., Schumann, 1989; Krol *et al.*, 2000]. However, in a recent study, Meeder and Nieuwstadt [2000] proposed to compute the subgrid reactant covariance by solving an extra equation for this quantity involving an eddy diffusivity subgrid flux model and closure models for the third order moments. In this paper, we present a subgrid model for the reactant covariance based on the scale similarity approach. We introduce a dynamic procedure to calculate the model coefficient based on information contained in the resolved scales. Such a procedure does not require any parameter specification or tuning. Finally, we test the model in simulations of a convective boundary layer (CBL) with a

chemical set-up consisting of an irreversible second-order reaction between two chemical species.

## 2. Dynamic Similarity Model

### 2.1. Model Formulation

[6] The filtered governing equation for the concentration of a reacting scalar that is solved in LES reads:

$$\frac{\partial \tilde{A}}{\partial t} + \tilde{u}_i \frac{\partial \tilde{A}}{\partial x_i} = -\frac{\partial Q_{A,i}}{\partial x_i} - k(\tilde{A}\tilde{B} + \chi) \quad (1)$$

where  $\tilde{A}$  is the spatially filtered (at scale  $\Delta$ ) concentration of the reactant  $A$ , here involved in the second-order reaction  $A + B \xrightarrow{k} \text{Product}$ . The effect of the unresolved scales on the evolution of the filtered scalar concentration appears through the subgrid-scale (SGS) flux  $Q_{A,i}$  and the SGS reactant covariance  $\chi$ . Notice that a similar equation is solved for the reacting scalar  $B$  since it is coupled with  $A$  through the chemical term.

[7] The SGS flux is defined as

$$Q_{A,i} = \tilde{u}_i \tilde{A} - \tilde{u}_i \tilde{A}, \quad (2)$$

and the SGS reactant covariance  $\chi$  that accounts for the mixing of the reactant at subgrid scales is

$$\chi = \tilde{A}\tilde{B} - \tilde{A}\tilde{B}. \quad (3)$$

Subgrid-scale models originally designed for potential temperature or moisture are currently used to parameterize the subgrid reactant flux whereas  $\chi$  is usually neglected.

[8] Similarity arguments are used to derive an expression for the subgrid covariance of reactants  $\chi$ . Similarity models assume that the structure of turbulent eddies at scales smaller than  $\Delta$  is similar to that at resolved scales slightly larger than  $\Delta$ . The subgrid covariance is set to be proportional to the resolved covariance at larger scales (typically between  $\Delta$  and  $2\Delta$ ). The subgrid covariance can then be expressed as

$$\chi = C_{sim}^\Delta (\overline{\tilde{A}\tilde{B}} - \overline{\tilde{A}}\overline{\tilde{B}}), \quad (4)$$

where the overline represents spatial filtering at scale  $2\Delta$  and  $C_{sim}^\Delta$  is the similarity coefficient. Since this coefficient may depend on the chemical regime, and to avoid tuning or a-priori specification, it is evaluated directly from the resolved scales by using a dynamic procedure. For the scalar covariance, the dynamic procedure is based on the identity

$$\Upsilon = \Xi - \overline{\chi} = \overline{\tilde{A}\tilde{B}} - \overline{\tilde{A}}\overline{\tilde{B}} \quad (5)$$

where  $\Upsilon$  is a resolved covariance that can be determined using the resolved scales.  $\Xi = \overline{\tilde{A}\tilde{B}} - \overline{\tilde{A}}\overline{\tilde{B}}$  is the subgrid covariance at a test-filter scale generally equal to  $2\Delta$ . Using the similarity model to compute  $\Xi$  and substituting (4) in (5) gives

$$\Upsilon = C_{sim}^{2\Delta} (\widehat{\tilde{A}\tilde{B}} - \widehat{\tilde{A}}\widehat{\tilde{B}}) - C_{sim}^\Delta (\overline{\tilde{A}\tilde{B}} - \overline{\tilde{A}}\overline{\tilde{B}}), \quad (6)$$

where the hat represents for the filtering procedure applied at scale  $4\Delta$ . In order to optimize the value of the model coefficient by combining equations (5) and (6), one needs to assume a functional relationship between  $C_{sim}^{2\Delta}$  and  $C_{sim}^\Delta$ . As a first approximation, here we assume that  $C_{sim}^{2\Delta} = C_{sim}^\Delta$ . Assuming this scale invariance of the model coefficient gives

$$\Upsilon = C_{sim}^\Delta X, \quad (7)$$

with

$$X = \left( \widehat{\tilde{A}\tilde{B}} - \widehat{\tilde{A}}\widehat{\tilde{B}} \right) - \left( \overline{\tilde{A}\tilde{B}} - \overline{\tilde{A}}\overline{\tilde{B}} \right). \quad (8)$$

Minimizing the error associated with the use of the similarity model in (5) results in

$$C_{sim}^\Delta = \frac{\langle \Upsilon X \rangle}{\langle XX \rangle}, \quad (9)$$

where the brackets  $\langle \rangle$  represent averaging over horizontal planes. At every time step and vertical position in the flow, the similarity coefficient is computed based on the resolved concentration using (9). The SGS covariance  $\chi$  is then calculated from (4) and used to obtain the total chemical term as shown in (1). It is important to note that this procedure is equivalent to using

$$-k(\tilde{A}\tilde{B} + \chi) = -k\left(1 + \frac{\chi}{\tilde{A}\tilde{B}}\right)\tilde{A}\tilde{B} = -k_{eff}\tilde{A}\tilde{B} \quad (10)$$

where  $k_{eff}$  is an effective reaction rate that includes the effect of the subgrid covariance. It is computed here with the dynamic similarity model.

### 2.2. Numerical Simulations

[9] The code used is a modified version of three-dimensional LES code described by *Albertson and Parlange* [1999], *Porté-Agel et al.* [2000], and *Porté-Agel* [2004]. A chemical solver has been implemented following *Vilà-Guerau de Arellano and Cuijpers* [2000]. The code uses a mixed pseudospectral finite-difference method and the subgrid-scale stresses and fluxes are parameterized with scale-dependent dynamic models. Test filtering for dynamic models is done using two-dimensional spectral cutoff filters. We simulate a dry convective atmospheric boundary layer driven by both thermal and shear forcing. We prescribe a uniform surface sensible heat flux of  $0.05 \text{ K.m.s}^{-1}$ . The initial potential temperature is  $311 \text{ K}$  up to  $700 \text{ meters}$  with an overlying inversion of strength  $0.006 \text{ K.m}^{-1}$ . The computational domain is of size  $(L_x, L_y, L_z)$  and it corresponds to a prescribed grid of  $N \times N \times N$  uniformly spaced points. The height of the domain is  $L_z = 1500 \text{ meters}$  and  $L_x = L_y = 2\pi L_z$ . High, medium and low resolutions (HR, MR and LR) are used with  $N = 96, 48,$  and  $16$  respectively. Periodic lateral boundary conditions are assumed. The maximum time step used in the calculation is  $0.5 \text{ s}$ . The simulations cover a  $1.5 \text{ hours}$  period and the statistics presented here are obtained averaging the results over the last hour. The convective velocity scale  $w_*$ , the friction velocity  $u_*$ , and the CBL height  $z_i$  are equal to  $1.07 \text{ ms}^{-1}$ ,  $0.3 \text{ ms}^{-1}$ , and  $750 \text{ m}$ , respectively.

[10] Two reactants are involved in the irreversible second-order reaction



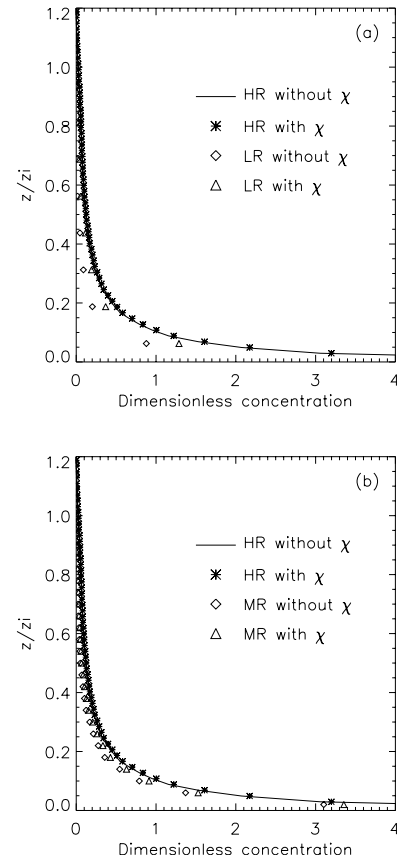
with a reaction rate coefficient  $k$  of  $2.1 \times 10^{-2} \text{ ppb}^{-1} \text{ s}^{-1}$ . The reactant  $A$ , so-called bottom-up reactant, is uniformly emitted at the surface with a flux of  $0.25 \text{ ppb.m.s}^{-1}$  and zero initial concentration in the CBL.  $B$  is not emitted and its initial profile shows a constant value of 2 ppb both in the CBL and in the free troposphere. The reaction rate coefficient and species concentrations are on the same order of magnitude as those found in the ABL [Krol *et al.*, 2000].

[11] The ratio between the turbulent integral time scale and the chemical time scale, i.e., the turbulent Damköhler number  $Da_t$ , is used to estimate the influence of turbulence on chemical transformations [Schumann, 1989; Sykes *et al.*, 1994; Vilà-Guerau de Arellano, 2003].  $Da_t$  is a measure the relative importance of the dynamical and chemical contributions to the governing equations of the mean reacting scalar concentrations. For reacting flows with  $Da_t \ll 1$ , the reactants are homogeneously mixed in the boundary layer. There is little influence of the turbulent structures on the chemistry. The reacting flow is in a slow chemistry regime. High above the threshold value of  $Da_t = 1$ , the reacting flow is in a fast chemistry regime. The chemistry is so active that the chemical species are almost not affected by the turbulent structure of the CBL. Between these limiting behaviors, e.g., for moderate chemistry, the turbulent mixing is expected to have a non-negligible impact on chemical transformations.

[12] By calculating the Damköhler number for  $A$  ( $Da_{t,A}$ ), we found that the bottom-up reactant  $A$  is in a fast chemical regime ( $Da_{t,A} \approx 14$ ). In such a flow, the behavior of  $A$  is dominated by the chemistry through the overall chemical contribution (resolved plus subgrid terms in the case of LES) included in the governing equation for its concentration. Therefore, any difference in  $A$  concentrations between the HR, MR and LR experiments is expected to be due to limitations in the treatment of the chemistry. For  $B$  (with  $Da_{t,B} < 0.1$ ), the turbulent structure of the CBL is not affecting its reactivity and its governing equation is dominated by the dynamical terms (resolved plus subgrid turbulent fluxes). Since we are interested in the effect of the unresolved scales on the chemical transformations, our analysis is restricted to the bottom-up scalar  $A$ .

### 3. Results and Discussion

[13] Vertical profiles of the mean reactant concentrations from the simulations with and without subgrid chemistry term for the three different resolutions (HR, MR and LR) are shown in Figure 1. In Figures 1a and 1b, results are presented from the LR and MR resolutions, respectively, and compared with the HR ones. The results from both HR simulations (solid lines and stars) suggest that for this chemical set-up, the subgrid segregation between the reactants has no significant influence on the reactant concentration for simulations with a number of grid points equal or higher than  $96 \times 96 \times 96$ . For the other resolutions, the profiles obtained when no subgrid model is used (diamonds in Figure 1) are significantly different from the ones



**Figure 1.** Vertical profile of dimensionless bottom-up reactant mean concentration. (a) HR, LR experiments without (with) computing the subgrid reactant covariance  $\chi$  are represented with solid line (star) and diamonds (triangles), respectively. (b) same as (a) but for the HR and MR experiments. The values are made dimensionless by the concentration scale  $a_*$  defined as the ratio of the surface flux of  $A$  to the convection velocity scale.

corresponding to the HR simulations. These differences can be larger than 50%. The main reason for this discrepancy is that the reactants are not uniformly distributed at subgrid scales during the lower resolution experiments and, consequently, the assumption of perfect mixing at those scales is not valid. Therefore, the use of the product of the reaction rate coefficient  $k$  (determined at the laboratory under perfect mixing conditions) together with the resolved concentrations as chemical term in (1) (i.e.,  $\chi = 0$ ) leads to an overestimation of the magnitude of the chemical rate. As a result, the reactant  $A$  is depleted too fast and important differences are noticed with respect to the HR experiment.

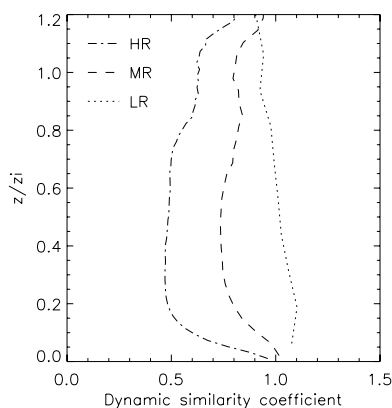
[14] The use of the subgrid model ( $\chi \neq 0$ ) affects strongly the results from the LR and MR experiments (triangles in Figure 1), e.g., more than 50% and between 10 and 20% increases of the mean concentrations, respectively. Their agreement with the HR experiment is largely improved. We found that the dynamic similarity coefficient  $C_{sim}^{\Delta}$  is very close to 1 throughout the CBL for the LR experiment (Figure 2). A similar value is found for the MR and HR experiments close to the surface and the top of the CBL. In the bulk, the dynamic coefficient shows values smaller than 1 (0.8 for MR and 0.5 for HR), revealing some

scale dependence. This is in contradiction to the assumption of scale invariance of the dynamic model coefficient. Accounting for this in the dynamic model would require relaxing the assumption of scale invariance and developing a scale-dependent dynamic model similar to the one of *Porté-Agel* [2004] for the subgrid fluxes. However we choose not to add that level of complexity (and computational cost) since scale dependence is only important when the subgrid chemistry effects are very small. Those effects are indeed negligible for HR in the bulk of the CBL as shown in Figure 3.

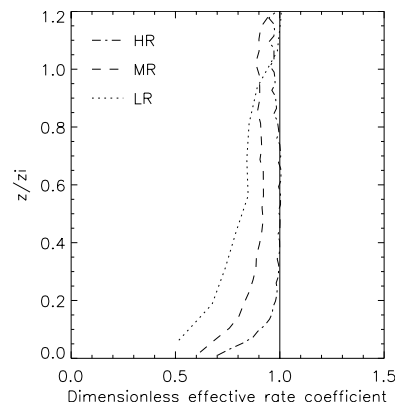
[15] In Figure 3, the vertical profiles of the normalized effective reaction rate  $k_{eff}/k$  are presented. This ratio is smaller than one due to the fact that the effective reaction rate coefficient  $k_{eff}$  is smaller than the reaction rate obtained under perfect mixing laboratory conditions,  $k$ . However, the  $k_{eff}$  that is calculated using the similarity coefficient during the HR experiment is very close to  $k$  in the bulk of the CBL. This suggests that for this chemical set-up at this resolution, the assumption of perfect mixing at subgrid scale is valid. As a result, similar reactant profiles are found if the subgrid reactant mixing model is used or not (see Figure 1). For the LR experiment,  $k_{eff}/k$  is as small as 0.5 in the surface layer, and it increases to 0.8 in the bulk of the CBL, meaning that the reaction rate is lowered by 50% and 20%, respectively, by the heterogeneous mixing at small scales. In the MR simulation,  $k_{eff}/k$  is larger throughout the boundary layer due to the fact that subgrid chemistry effects become relatively smaller with increasing resolution. In particular,  $k_{eff}$  varies from about  $0.7k$  in the surface layer to  $0.9k$  in the bulk of the boundary layer. The reduction in reaction rate is a direct consequence of accounting for the non-zero contribution of the subgrid covariance  $\chi$  through the dynamic similarity model. Failing to account for this term is expected to overestimate the reaction rate and, in turn, deplete the concentration of the reactant to unrealistic, scale-dependent levels, as illustrated in Figure 1.

#### 4. Conclusions

[16] In this study, we have developed and implemented a similarity model for the subgrid reactant covariance to be used in large-eddy simulations of atmospheric reacting



**Figure 2.** Vertical profile of the dynamic similarity coefficients. The dot-dashed, dashed and dotted lines account for the HR, MR and LR experiments, respectively.



**Figure 3.** Vertical profile of the ratio of the effective reaction rate to the reaction rate coefficients ( $k_{eff}/k$ ). The dot-dashed, dashed and dotted lines account for the HR, MR and LR experiments using  $\chi$ , respectively. The solid line represents the dimensionless reaction rate coefficient calculated at the laboratory, i.e.,  $\chi = 0$ .

flows. The model coefficient is computed during the simulations using a dynamic procedure that is based on the resolved reactant concentrations and that does not require any parameter specification or tuning.

[17] Our results show that subgrid effects on the chemical transformation of reacting scalars can be important. We found that neglecting these effects can lead to substantial overestimation of the reactants depletion rates and, consequently, an underestimation of their concentrations.

[18] By using the dynamic similarity model to determine the subgrid reactant covariance  $\chi$  included in the chemical term, our LES code is able to account for the effect of the unresolved scales on the chemical transformations. We define an effective reaction rate coefficient that incorporates the subgrid covariance effects and that can be used instead of the reaction coefficient obtained in the laboratory under perfect mixing conditions. Further studies will address the variability and, in particular, the issue of scale dependence of the model coefficient with respect to the chemical regime. We will also explore the use of a Damköhler number based on subgrid-scale time scales to quantify the relative importance of the subgrid-scale chemistry as a function of both resolution and chemical regime.

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