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Key Points:
- A EDMF model can well reproduce the results of a LES embedded with idealized aqueous reactions
- The aqueous oxidation of SO2 by H2O2 is relatively slow compared to the in-cloud residence time of air parcels
- Operator splitting between tracer transport and aqueous reactions leads to significant errors

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Representing effects of aqueous phase reactions in shallow cumuli in global models

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Abstract
Aqueous phase reactions are important, sometimes dominant (e.g., for SO2), pathways for the oxidation of air pollutants at the local and/or global scale. In many current chemical transport models (CTMs), the transport and aqueous reactions of chemical species are treated as split processes, and the subgrid-scale heterogeneity between cloudy and environmental air is not considered. Here using large eddy simulation (LES) with idealized aqueous reactions mimicking the oxidation of surface-originated SO2 by H2O2 in shallow cumuli, we show that the eddy diffusivity mass flux (EDMF) approach with a bulk plume can represent those processes quite well when entrainment/detrainment rates and eddy diffusivity are diagnosed using a conservative thermodynamic variable such as total water content. The reason is that a typical aqueous reaction such as SO2 aqueous oxidation is relatively slow compared to the in-cloud residence time of air parcels in shallow cumuli. As a result, the surface-originated SO2 is well correlated with and behaves like conservative thermodynamic variables that also have sources at the surface. Experiments with various reaction rate constants and relative abundances of SO2 and H2O2 indicate that when the reaction timescale approaches the in-cloud residence time of air parcels, the errors of the bulk plume approach start to increase. Treating chemical tracer transport and aqueous reaction as split processes leads to significant errors, especially when the reaction is fast compared to the in-cloud residence time. Overall, the EDMF approach shows large improvement over the CTM-like treatments in matching the LES results.

1. Introduction
Moist convection plays a number of roles in atmospheric chemistry including vertical transport and turbulent mixing of chemical species, photochemistry (by altering the radiation field), lightning production of NOx, wet removal, and aqueous phase reactions. The aqueous phase reactions are very important for some chemical species, a prominent example being sulfur dioxide (SO2). SO2 has major sources from fuel combustion, ore smelting, volcano eruptions, and oxidation of dimethyl sulfide (DMS) emitted by the marine biosphere. SO2 can be oxidized in the atmosphere, producing sulfate aerosols that affect air quality, cloud nucleation, and climate [e.g., Berg et al., 2011; Ghan et al., 2012]. Because the aqueous phase oxidation of SO2 by H2O2 and O3 is much more rapid than the gaseous phase oxidation by OH, it dominates global sulfate aerosol formation (60%–80%) [e.g., Barth et al., 2000; Rasch et al., 2000; Benkovitz et al., 2006; Wang et al., 2011]. Thus, it is important to appropriately represent this type of aqueous phase reaction in global models.

In current chemical transport models (CTMs; and global climate models, GCMs, with chemistry components), due to their coarse resolution, shallow cumuli are parameterized, as are the associated aqueous phase reactions. In many CTMs [e.g., Barth et al., 2000; Liu et al., 2005; Jöckel et al., 2006; Verma et al., 2007; Wu et al., 2007], the transport and reactions of chemical tracers are treated as split processes over a CTM time step: the CTMs first use the convective mass flux to calculate the convective transport then call chemical solvers to calculate the gaseous and aqueous phase reactions. In addition, the chemical solvers usually use the CTM grid mean chemical concentrations to calculate the aqueous phase reactions. The subgrid-scale heterogeneity (e.g., the difference between cloudy and clear-sky regions) of chemically reactive tracers and their correlations is not considered. The above two simplifications are justifiable for gaseous phase reactions that occur throughout a grid cell but are less justifiable for aqueous phase reactions. Aqueous phase reactions in cumuli
mainly occur in cloudy updrafts, in which the concentrations of chemical tracers can be quite different from the grid mean concentrations, as shown in both observations [e.g., Daum et al., 1984] and numerical modeling [e.g., Kazil et al., 2011]. The cloudy updrafts also contribute to the majority of the tracer transport above the subcloud layer [e.g., Vilà-Guerau de Arellano et al., 2005], thereby coupling the chemical transport and reactions together.

The objective of this study is to improve representations of aqueous phase reactions in shallow cumuli in the global models, particularly to mitigate the errors due to the above two simplifications. We incorporate an idealized aqueous reaction into the large eddy simulation (LES) of shallow cumuli. LES has been used by many previous studies to investigate the effects of convection on chemistry, e.g., the photochemical disequilibrium in the dry boundary layer [Krol et al., 2000] and the transport and transformations influenced by shallow cumulus [Vilà-Guerau de Arellano et al., 2005; Kim et al., 2012]. Here the LES resolves the turbulent flow and the aqueous reaction in the shallow cumuli at the cloud scale, which serves as the ground truth. The idealized chemical reaction is easy to understand and can be used as a starting point for the investigation of more complex chemical reactions in the future. We then assess whether a simple convective parameterization (the eddy diffusivity mass flux approach, EDMF, with a bulk plume model, simply called the EDMF model hereafter) with the aqueous reaction appropriately treated can well represent both the chemical and thermodynamic aspects at the same time.

Most convective parameterizations are designed to represent and are validated against the thermodynamic aspect of convection, such as heat and moisture, or inert chemical transport. Less evaluation has been done of the chemically reactive tracers, although the simulations of chemistry in global models are sensitive to the choices of convective parameterizations [e.g., Jacob et al., 1997; Easter et al., 2004; Lawrence and Philip, 2005]. To separate out the uncertainties in representing chemistry from the uncertainties in parameterizing convection and clouds themselves, we diagnose the parameters of the EDMF model from the LES results. The aqueous reaction is formulated within the EDMF model in a way that improves upon the above two simplifications (operator splitting and neglecting subgrid-scale heterogeneity of chemicals). We show that this representation of the aqueous reaction within the EDMF model can well reproduce the LES-simulated chemical aspect over a wide range of chemical regimes, thus making it an effective way to represent aqueous reactions and transport in shallow cumuli. We also analyze the errors of aqueous reaction in the EDMF model, which helps us understand and qualitatively assess when the EDMF model is adequately accurate and when it is not.

2. Methodology and Experimental Design

2.1. The LES With Reactive Tracers

The shallow cumuli case is the nonprecipitating oceanic trade cumulus case from the undisturbed Barbados Oceanographic and Meteorological Experiment (BOMEX) [Holland and Rasmusson, 1973]. The BOMEX shallow cumuli stayed in a steady state for 5 days in the field observation without apparent complications from precipitation or large-scale perturbations. It is an excellent test bed for us to focus on the chemical aspect, because the convective processes are relatively simple and well studied. The LES is the System for Atmospheric Modeling (SAM) [Khairoutdinov and Randall, 2003], which has been used to simulate the BOMEX case [e.g., Siebesma et al., 2003; Nie and Kuang, 2012a]. We run SAM with a spatial resolution of 25 m in all directions in a domain of 6.4 km (x) × 6.4 km (y) × 3 km (z) with doubly periodic horizontal boundary conditions and a time step of 1 s. The forcing and other settings are the same as the intercomparison study of BOMEX described in Siebesma et al. [2003].

Two massless tracers, $\phi_1$ and $\phi_2$, with units of parts per billion, are added to the LES to mimic the aqueous oxidation of SO$_2$ by H$_2$O$_2$. $\phi_1$ is released from the surface with a constant flux $F_{sfc,\phi_1}$, which mimics the atmospheric oxidant H$_2$O$_2$, is relaxed to a reference profile $\phi_{2,ref}$ that is constant in height. We set the relaxation time of $\phi_2$ to be 1 day based on photochemical production of H$_2$O$_2$ [Jacob et al., 1990]. $\phi_1$ is also relaxed to zero with a 1 day relaxation time, which may be viewed as representing gaseous phase oxidation, such as by OH [Barth et al., 2000] or O$_3$ in sea-salt aerosols [Alexander et al., 2005]. The relaxation of $\phi_1$ and $\phi_2$ is only applied in clear-sky grid cells. We limit this study to surface-originated $\phi_1$, which may be viewed as anthropogenic sources of SO$_2$ or other pollutants. Other possible sources, such as the oxidation of DMS, will be considered in future work.
\( \phi_1 \) and \( \phi_2 \) react in cloud droplets within cloudy grids (grid cells with cloud liquid water \( q_c \geq 0.01 \text{ g kg}^{-1} \)). The rate of the aqueous reaction can be expressed in their gaseous phase concentrations with a bulk reaction constant \( k \)

\[
R_n = - \frac{d\phi_{1,n}}{dt} = - \frac{d\phi_{2,n}}{dt} = k\phi_{1,n}\phi_{2,n}q_{c,n},
\]

where the subscripts \( n \) indicate that they are for individual LES grid cells. \( k \) (with a unit of \( \text{s}^{-1} \text{ ppb}^{-1} \text{ per g kg}^{-1} \) of cloud liquid water; unit is omitted hereafter) is the product of the aqueous reaction rate constant in liquid water and Henry's equilibria constants (including the dissociation of \( \text{SO}_2 \) in the aqueous phase). The aqueous reaction rate constant is divided by the liquid water content, while the conversion from aqueous phase concentrations to gas phase concentrations is multiplied by the liquid water content. Thus, \( k \) in equation (1) has no dependence on \( q_{c,n} \). For the aqueous oxidation of \( \text{SO}_2 \) by \( \text{H}_2\text{O}_2 \), \( k \) is about \( 1-2 \times 10^{-3} \) [Seinfeld and Pandis, 1998]. Its dependence on the \( \rho \) value is small and neglected. As in many previous studies [e.g., Schumann, 1989; Vilà-Guerau de Arellano et al., 2005], the chemical reaction here is highly idealized. However, the minimal complexity of the chemistry allows us to better understand the influences of convection on chemistry and to improve its representation in parameterizations.

A control case is set up as the benchmark. The parameters \( F_{sfc,\phi_1} \) and \( \phi_{2,\text{ref}} \) determine the relative abundances of \( \phi_1 \) and \( \phi_2 \). In the control case, we set \( F_{sfc,\phi_1} = 0.024 \text{ ppb kg m}^{-2} \text{ s}^{-1} \) and \( \phi_{2,\text{ref}} = 0.9 \text{ ppb} \) (subscript 0 indicates the control case value), so that the concentrations of \( \phi_1 \) and \( \phi_2 \) are comparable in cloudy updrafts. Observations show that either \( \text{SO}_2 \) or \( \text{H}_2\text{O}_2 \) can dominate depending on the environment [Daum et al., 1984]. The control case \( k \) is set to be \( 10^{-3} \), close to the representative value for \( \text{SO}_2 \) aqueous oxidation by \( \text{H}_2\text{O}_2 \).

To explore and evaluate the performance of the EDMF model in a wide range of situations, two groups of experiments are carried out in addition to the control case. Cases in group 1 have the same \( k = 10^{-3} \) as in the control case. However, in each case \( \phi_{2,\text{ref}} \) is divided and the control case \( F_{sfc,\phi_1} \) is multiplied by the same factor. There are a total of 12 cases with this factor varying from \( \frac{1}{12} \) to 12. Experiments in this group cover \( \text{SO}_2 \) aqueous oxidation in different chemical regimes, from \( \text{SO}_2 \) dominant \((\phi_{2,\text{ref}}/\phi_{2,\text{ref0}} \ll 1) \) to \( \text{H}_2\text{O}_2 \) dominant \((\phi_{2,\text{ref}}/\phi_{2,\text{ref0}} \gg 1) \). In the second group of 12 experiments, we keep \( F_{sfc,\phi_1} \) and \( \phi_{2,\text{ref}} \) the same as in the control case but change \( k \) from \( 10^{-4} \) to \( 10^{-1} \). Experiments in this group extend our study to explore a range of aqueous phase reaction rates.

The initial conditions of the chemical tracers are \( \phi_1 \) being zero and \( \phi_2 \) being its reference profile. For most of the paper, we focus on the comparison between the EDMF model and the LES results in the chemical steady state to reduce the dependence on the initial conditions of chemical tracers. In section 3.6, we examine the first several hours after initialization to examine the EDMF model's performance in chemical transient state. Many LES, including SAM, can sustain a quasi-steady BOMEX convection only for several hours (hours 2–6 after the initialization; after that the thermodynamic fields slowly drift away) [e.g., Siebesma et al., 2003], which is far less than the observed 5 days and too short to reach a chemical steady state without appropriate initial profiles of the chemical tracers. To overcome this limitation, we first run the model for 2 h. We then restart and run the model repeatedly from the end of hour 2 to the end of hour 6 from the same restart file (saved at the end of hour 2) except with a different set of Gaussian random noise applied to the temperature fields of the lowest five levels in each of the restarted runs. The added noise has a standard deviation of 0.02 K. \( \phi_1 \) and \( \phi_2 \) averaged over the clear sky and cloudy air are calculated at each height during the last hour of a previous run. Then, the clear sky and cloudy means are assigned as the initial values of \( \phi_1 \) and \( \phi_2 \) in the clear sky and cloudy air, respectively, of the following restarted run. We iterated this procedure for more than 12 rounds (48 simulation hours) for each case and confirmed that the chemical steady state is reached. Snapshots of thermodynamic (temperature \( T \), total water content \( q_t \), and others) and chemical variables \((\phi_1, \phi_2, R)\) are saved every minute during the final run for analysis. The first 30 min simulation of the final run is discarded as spin-up, so that heterogeneities of \( \phi_1 \) and \( \phi_2 \) inside clouds and clear sky are fully developed for the analysis period.

2.2. The EDMF Model

The EDMF model is evaluated against the LES results. Consider the budget equation of an arbitrary tracer \((\psi)\) horizontally averaged over the LES domain (denoted by overbar)

\[
\frac{\partial \bar{\psi}}{\partial t} = \left( \frac{\partial \bar{\psi}}{\partial t} \right)_{\text{forcing}} - \frac{1}{\rho} \frac{\partial F_\psi}{\partial z} + \mathbf{\nabla} \cdot \mathbf{q}. \tag{2}
\]
Figure 1. The LES-simulated (a) active updrafts area fraction $a$ and mass flux $M$, (b) $q_{cu}$, (c) total water content $q_t$ in updrafts and environment, (d) $F_{qt}$ and its decomposition, (e) $\epsilon$ and $d$ diagnosed from $q_t$, and (f) $K$ diagnosed from $q_t$, $\phi_1$, and $\phi_2$. The dashed line indicates values in the subcloud layer.

$\rho$ is air density. The terms on the right-hand side (RHS) are the imposed large-scale forcing, vertical convergence of turbulent flux, and net source, respectively. For the chemical tracers, the large-scale forcing term is zero, and the source terms include relaxation in the clear sky and the aqueous reaction in cloudy air.

By separating active updrafts from the environment [e.g., Siebesma and Cuijpers, 1995], the turbulent flux can be written as

$$F_\psi = \rho w' \psi' = \rho a(1-a)(w_u - w_e)(\psi_u - \psi_e) + \rho a w' \psi'' + \rho (1-a) w' \psi''',$$

(3)

where subscripts $u$ and $e$ indicate conditional averaging over active updrafts and the environment, respectively, $w$ is the vertical velocity and $a$ is the area fraction of active updrafts. Since $a$ is very small for the BOMEX case (Figure 1a), we adopt the following highly accurate approximation in the rest of the paper: $(1-a) \approx 1$ and $\psi_e \approx \bar{\psi}$. The first term on the RHS of equation (3) represents net transport by active updrafts and the compensating subsidence. Under the above approximation, it can be written as $M(\psi_u - \bar{\psi})$, where $M = \rho a w_u$ is the convective mass flux. The second and third terms represent turbulent flux due to heterogeneities inside updrafts and the environment, respectively.

The EDMF model [e.g., Siebesma et al., 2007; Sušelj et al., 2012] parameterizes $F_\psi$ as the sum of a mass flux (MF) component and an eddy diffusivity (ED) component,

$$F_\psi \approx M(\psi_u - \bar{\psi}) - \rho K \frac{\partial \bar{\psi}}{\partial z},$$

(4)
where $K_v$ is the eddy diffusion coefficient. To describe the MF component in the EDMF approach, we use a bulk plume model [e.g., Siebesma et al., 2007]

$$\frac{1}{M} \frac{\partial M}{\partial z} = e_u - d_u,$$  

(5)

$$\frac{\partial M\psi_u}{\partial z} = e_u M\psi - d_u M\psi_u + \rho S_{\psi u},$$  

(6)

where $e$ and $d$ (m$^{-1}$) are the effective fractional entrainment and detrainment rates, respectively. In the cloud layer, the active updrafts are defined as cloudy grids with upward vertical velocity ($q_u > 0.01$ g kg$^{-1}$ and $w > 0$ m s$^{-1}$). In the subcloud layer, they are defined as grids with $w$ values in the top 1.3% percentile, which is within the range (1%–5%) suggested by Siebesma et al. [2003, 2007]. Sušelj et al. [2012] tested that the overall results of their EDMF model are fairly insensitive to the specified threshold of the percentile. The tracers in the updrafts have initial values at the lowest model level ($z_1$) as the horizontal mean added with an excess that scales with the surface flux ($F_{u\text{,sfc}}$),

$$\psi_u(z_1) = \bar{\psi}(z_1) + a \frac{F_{u\text{,sfc}}}{\sigma_w(z_1)},$$  

(7)

where $\sigma_w$ is the standard deviation of $w$ and $a = 1.06$ is a scaling parameter from Siebesma et al. [2007]. Given the $\psi$ values at the lowest level, we can integrate equations (5)–(6) upward to have the $\psi_u$ values on all levels. Compared to many other parameterizations that treat the cloud layer and the subcloud layer separately, the EDMF model has the advantage of providing a unified framework that connects the subcloud layer and the cloud layer smoothly. It has been operational in several GCMs and has shown significant improvements in the simulation of shallow clouds [e.g., marine stratocumulus and continental stratus, e.g., Koehler, 2005].

The prognostic variables of the EDMF model (equations (4)–(7)) are $q$, and the liquid water static energy ($h_l = C_p(T + gz - L_q)$, where $C_p$ is the specific heat at constant pressure and $L$ is the latent heat of vaporization) for the thermodynamic aspect and $\phi_1$ and $\phi_2$ for the chemical aspect. The EDMF model requires specifying the parameters $e_u$, $d_u$, and $K_v$ for each tracer. One can diagnose these parameters by matching the LES and EDMF model results (i.e., collecting $M$, $\bar{w}$, and $\psi_u$ from LES snapshots and solving equations (5)–(6) for $e_u$ and $d_u$, collecting $F_u$ from the LES and solving equation (4) for $K_v$ with $-\rho K_v \frac{\sigma_w}{\alpha u}$ treated as the residual). Siebesma et al. [2003] showed that because of the strong correlation between $q$ and $h_l$, their tracer parameters are very close to each other. Our analysis confirmed their conclusion: the normalized root-mean-square error between $e_q$ and $e_h$ is about 20%. As many parameterizations in CTMs do not have parameters for individual tracers, we evaluate the EDMF model with the same set of parameters diagnosed from $q$ for both thermodynamic and chemical tracers. By doing so, we are considering the scenario that the EDMF model can “perfectly” represent the thermodynamic aspects of convection and clouds; thus, any errors in the chemical variables are due to the parameter dependence on tracers and deficiencies in the representation of aqueous reaction.

### 2.3. Treatments of the Aqueous Phase Reactions in the EDMF Model and Current CTMs

Effects of the aqueous reaction are considered here only within cloudy updrafts ($R_u$, equivalent to $-S_{\psi u}$ in equation (6) for the reactive tracers), given the reaction rate in cloudy downdrafts being small. In the EDMF model, $R_u$ is calculated using variables in cloudy updrafts,

$$R_{u,\text{EDMF}} = k\phi_1 u \psi_2 q_{c,u}.$$

(8)

In other words, the effect of cloudy/clear-sky heterogeneity on the aqueous reaction is explicitly represented. Moreover, the transport and reactions of reactive tracers are calculated simultaneously as we integrate the bulk plume upward; therefore, they are coupled. In addition, the mass exchange of reactive tracers between the environment and cloudy updrafts is through entraining/detraining mixing processes, which are deduced from and constrained by the thermodynamic tracer.

The above representation of aqueous reaction is more consistent with the real atmospheric processes. With the transport (equations (4)–(6)) and the aqueous reaction (equation (8)) parameterized, we can run the EDMF as a single-column model using equation (2). At each time step, equations (5)–(6) and (8) are first integrated upward to obtain $\psi_u$ and $S_{\psi u}$. Next, equation (4) gives the convective flux $F_{u\psi u}$. This information is then used in equation (2) to calculate the tracer mixing ratio profiles of the following time step. Since the parameters
Parameterizations in current CTMs usually treat the transport and reactions of chemical tracers in shallow cumuli as split processes. The tracer transport by sub-CTM grid-scale convection and chemical reactions is calculated in separate modules. Moreover, it is common to use the CTM grid mean tracer concentrations to calculate the aqueous reaction in cloudy air,

\[ R_{\text{CTM}} = k \Phi_1 \Phi_2 q_{t,c,w} \]  

To estimate the potential errors due to process splitting in many CTMs, we run the EDMF single-column model as if the transport and reaction are separate as in the CTMs. Over a CTM time step \( \Delta t_{\text{CTM}} \), we first calculate the tracer transport tendencies using the EDMF model without aqueous reaction then calculate the tracer tendencies due to aqueous reaction using equation (9). The profiles of \( \Phi_1 \) and \( \Phi_2 \) are updated using the total tendencies over \( \Delta t_{\text{CTM}} \). Note that since we do not update tracer profiles during the split processes (as some CTMs do), the results do not depend on whether transport or aqueous reaction is calculated first. This is a more consistent comparison with the EDMF model. In section 3.5, the results from this setting are compared with the EDMF model with transport and aqueous reaction coupled.

### 3. Results

We start with some basic characteristics of the BOMEX shallow cumuli in the LES (Figure 1). The area fraction \( a \) (Figure 1a) of the active updrafts is specified to be a constant (1.3%) in the subcloud layer and decreases with height in the cloud layer. In the cloud layer, the net mass flux \( M \) also decreases with height but less than \( a \) because \( w_u \) increases with height due to buoyancy acceleration. At the cloud base (around 550 m level), \( a \) and \( M \) are discontinuous due to the different definitions of updrafts applied in the subcloud layer and the cloud layer. Although not for the reactive tracers examined here, for other tracers with strong vertical gradients near the cloud base, this discontinuity may induce biases in the EDMF model. \( q_{t,c,w} \) increases with height due to continuous condensation as cloudy updrafts rise (Figure 1b). The active updrafts are significantly moister than the environmental mean, especially in the cloud layer (Figure 1c). As cloudy updrafts rise, turbulent mixing continuously entrains environmental air into cloudy updrafts, pushing cloudy updrafts’ properties toward the environmental air properties. Figure 1d shows the flux of total water, \( F_{q_t} \), and its decomposition through equation (4). The convective flux of \( q_t \) is mostly due to the ED component in the subcloud layer, while mostly due to the MF component in the cloud layer. This supports the “mass flux approximation” used in many convective parameterizations that approximate the total flux by the MF component in the cloud layer. The EDMF model represents the residuals as an eddy diffusion process naturally connected with the subcloud layer eddy diffusion, which dominates the flux transport there.

Figures 1e and 1f show the parameters diagnosed from \( q_t \) and applied to the chemical tracers. In the cloud layer, the diagnosed \( \epsilon \) and \( d \) are consistent with results in previous studies [e.g., Siebesma et al., 2003]. In the subcloud layer, \( \epsilon \) and \( d \) are smaller, consistent with the relatively constant \( M \) in the subcloud layer. \( K_{\epsilon,\phi} \), which is close to the results in Figure 11 of Siebesma et al. [2003], is very large in the subcloud layer, corresponding to strong turbulent mixing there that maintains nearly constant vertical profiles of \( q_t \) (and other tracers). \( K_{\epsilon,\phi} \) is small in the cloud layer, corresponding to small ED flux there.

#### 3.1. The Control Case

Now we examine the steady state chemical aspect in the control case of the LES simulations (solid lines in Figure 2). The \( \Phi_1 \) profiles (Figure 2a) share similar features with the \( q_t \) profiles (Figure 1c), because the source of \( \Phi_1 \), like \( q_t \), comes from the surface flux and thus \( \Phi_1 \) is well correlated with \( q_t \). \( \Phi_1 \) and \( \Phi_2 \) are nearly constant with height in the subcloud layer due to the strong turbulent mixing there. \( \Phi_{1u} \) and \( \Phi_{2u} \) at the cloud base have similar values as \( \Phi_{1s} \) and \( \Phi_{2s} \) in the surface layer, because cloudy updrafts originate from the surface. Above the cloud base, \( \Phi_{1u} \) and \( \Phi_{2u} \) decrease with height due to the aqueous reaction and entrainment of environmental air having lower mixing ratios. Detrainment of \( \Phi_{1u} \)-depleted cloudy air leads to the decrease of \( \Phi_{2u} \) with height. This effect is balanced by the relaxation of \( \Phi_2 \) in the clear sky, leading to the intersection of \( \Phi_2 \) and \( \Phi_{2u} \) at around 800 m height.
Figure 2. The control case steady state (a) $\phi_1$ and $\phi_1 u$, (b) $\phi_2$ and $\phi_2 u$, (c) $F_{\phi_1}$ and its decomposition, (d) $F_{\phi_2}$ and its decomposition, and (e) aqueous reaction rate and its portion in cloudy updrafts and downdrafts. The color lines are the LES results, and the color circles are the EDMF model results.

The convective fluxes of $\phi_1$ and $\phi_2$ and their decomposition are shown in Figures 2c and 2d. $F_{\phi_2}$ is much smaller than $F_{\phi_1}$ in magnitude due to the small contrast of $\phi_2$ in updrafts and environment (Figure 2b). In the subcloud layer, the ED component dominates the total flux of both $\phi_1$ and $\phi_2$. In the cloud layer, the MF component accounts for almost all of the total flux for $\phi_1$. For $\phi_2$, the MF and ED components are of comparable amplitudes but with opposite signs. As can be seen from Figures 2c and 2d, the mass flux approximation is well satisfied for $\phi_1$, consistent with previous studies that examined the convective transport of surface-originated tracers [e.g., Vilà-Guerau de Arellano et al., 2005]. However, the approximation is not well satisfied for $\phi_2$, suggesting that additional considerations are needed for non-surface-originated tracers.

The horizontally averaged reaction rate $\bar{R}$ (Figure 2e) peaks slightly above cloud base and then decreases with height, mainly due to the decrease of cloud fraction with height (Figure 1a). $R_u$ actually increases with height due to the increase of $q_{w,c}$ (figure not shown). Aqueous reaction in cloudy updrafts ($\alpha R_u$) accounts for most of the total aqueous reaction. Thus, neglecting aqueous reaction in cloudy downdrafts in the EDMF model is an acceptable simplification for the shallow cumulus studied here. For other types of convection with substantial area fraction of cloudy downdrafts, such as stratocumulus, aqueous reaction in cloudy downdrafts should also be considered.

The steady state results of the EDMF model (circles in Figure 2) reproduce the LES results quite well. The matches of $\phi_1$ and $F_{\phi_1}$ are particularly good (vertically averaged relative errors <5%). The EDMF model
underestimates $R$ by about 11%, but this is mostly due to the neglect of the aqueous reaction in cloudy downdrafts. When compared to reactions only in cloudy updrafts ($aR_u$), the error in EDMF reduces to about 3%. The EDMF model also reproduces $\phi_2$ and $F_{\phi_2}$ (vertically averaged relative errors <5%), although, with some biases in the shape of the profiles. It underestimates the $\phi_2$ flux of the MF component in the upper levels and has almost zero ED $\phi_2$ flux in the cloud layer. Due to the cancelation of biases, the discrepancies of $F_{\phi_2}$ between the EDMF and LES results are, fortunately, smaller than discrepancies in the individual components.

Although the EDMF model well reproduces the LES results of the control case, in sections 3.2–3.4 we examine the underlying assumptions of the EDMF model that can lead to errors in representing chemical transports and aqueous reactions and understand the dependence of these errors under different chemical parameters or settings.

### 3.2. Errors in the Eddy Diffusivity Component

The EDMF model has nonnegligible deficiencies in parameterizing non-surface-originated tracer $\phi_2$ (Figures 2b and 2d). Particularly, it has almost zero ED flux component in the cloud layer, due to the small $K$ diagnosed from $q_s$. Figure 1f also shows $K$ diagnosed from $\phi_1$ and $\phi_2$. The diffusivities ($K$) of the surface-originated tracer $q_s$ and $\phi_1$ are close to each other. However, $K_{\phi_2}$ shows quite different features from $K_{q_s}$.

In the subcloud layer, $K_{\phi_2}$ is about half of $K_{q_s}$, but the differences of $K$ there do not affect the EDMF model too much. We have run the EDMF model with $K_{\phi_2}$ doubled or halved in the subcloud layer. The resulting $\phi_1$ and $\phi_2$ are very close to the ones shown in Figure 2. This is because in the subcloud layer, $K$ is so large that its first effect is to maintain nearly constant tracer profiles with height. The vertical gradient of tracers is relatively small ($\frac{\partial \phi}{\partial z} \approx 0$). Sizable changes in $K$ can easily be compensated by small adjustments of tracer vertical gradients in the model. The $K$ parameter may be important for the thermodynamic variables ($h_l$ and $q_s$), which in turn can affect the subcloud layer properties, such as the subcloud layer depth and the delicate convective inhibition near the cloud base. However, for passive chemical tracers that do not interact with convection, using $K$ diagnosed from $q_s$ is sufficient for parameterizing them in the subcloud layer.

In the cloud layer, $K_{\phi_2}$ has a singular point near the 1300 m level, corresponding to the local minimum of $\phi_2$ there (Figure 2b). Above that level, $K_{\phi_2}$ is negative, which is unphysical. Note that the “ED” flux in the LES (Figure 2d) is actually calculated as the difference between the total flux and the flux due to the MF component. As seen from equations (3)–(4), the EDMF model posits that $\rho a w' \phi'_2 + \rho (1-a) w' \phi'_e \approx -\rho K_{\phi_2} \frac{\partial \phi_2}{\partial z}$, under the assumptions that $\rho a w' \phi'_2$ is small and the turbulence in the environment is random. Figure 3 shows that $\rho w' \phi'_2$ is relatively small. The positive $\phi_2$ flux of the ED component (and thus the negative $K_{\phi_2}$) is mostly due to transport in the subsiding shells (Figure 3), which is defined here as grids within 200 m of the nearest cloudy updrafts edge, including both saturated and unsaturated air [Heus and Jonker, 2008]. The flux in the rest of the environment (quiescent environment) is very small. If we further increase the cloud shell size, for example, to within 400 m of the updrafts edge, the $\phi_2$ flux in the quiescent environment becomes slightly negative and follows the $\phi_2$ gradient as eddy diffusion. The above analysis suggests that for

![Figure 3](image_url)
non-surface-originated tracer $\phi_2$, the eddy diffusion cannot appropriately represent the non-MF component flux, and the subsiding shells of the shallow cumulus clouds should be included in the parameterization.

### 3.3. Errors Due To In-Cloud Heterogeneities

Next, we move to the MF component (i.e., the bulk plume model) of the EDMF model, particularly the aqueous reaction rate in the cloud layer. The bulk plume model assumes that the environment and cloudy updrafts have uniform properties within each category (the top-hat approximation) [Siebesma and Cuijpers, 1995]. In other words, the bulk plume model explicitly distinguishes cloudy updrafts from the environment but neglects the heterogeneities of air within cloudy updrafts and the environment, leading to errors in the calculation of the aqueous reaction. To estimate the relative importance of the heterogeneity within cloudy updrafts, we define a segregation error ($\gamma_{\text{seg}}$ with units of percent) as the relative error due to the top-hat approximation when the cloudy updraft mean properties are correctly predicted,

$$
\gamma_{\text{seg}} = \frac{\phi_{1u} \phi_{2u} q_{c,u} - \phi_{1c} \phi_{2c} q_{c,n}}{\phi_{1n} \phi_{2n} q_{c,n}} - 1.
$$

Neglecting second-order terms, $\gamma_{\text{seg}}$ can be written as

$$
\gamma_{\text{seg}} \approx -C_{\phi_1,2} \mu_{\phi_1} \mu_{\phi_2} - C_{\phi_1,2} \mu_{\phi_1} \mu_{\phi_2} - C_{\phi_1,\phi_2} \mu_{\phi_1} \mu_{\phi_2},
$$

where $C_{x,y}$ is the correlation coefficient between $x$ and $y$ and $\mu_x$ is the coefficient of variation (the ratio of the standard deviation to the mean) of $x$. $\gamma_{\text{seg}}$ with the opposite sign is very close to the intensity of segregation used in many previous studies [e.g., Krol et al., 2000; Vilà-Guerau de Arellano et al., 2005]. Here the segregation of tracers in clear-sky and cloudy updrafts is already taken into account in the bulk plume model, so that $\gamma_{\text{seg}}$ measures segregation of tracers inside cloudy updrafts.

The decomposition of $\gamma_{\text{seg}}$ in the LES control case based on equation (11) is shown in row 1 of Figure 4. First, we examine the correlation coefficients in Figure 4 (row 1, middle column). $\phi_1$ is strongly positively correlated with $q_c$ in cloudy updrafts ($C_{\phi_1,q_c}$ is close to 1), as expected. $\phi_2$ and $q_c$ are also positively correlated near the cloud base, implying that the most energetic subcloud-layer updrafts are enriched in the reactive tracers and moisture. As cloudy updrafts rise, the aqueous reaction of the reactive tracers with each other leads to the negative correlation between $\phi_1$ and $\phi_2$. In addition, above the height where $\phi_{2u}$ and $\phi_2$ intersect (around 800 m, Figure 2b), entrainment has opposite effects on $\phi_2$ and $\phi_1$ of cloudy updrafts: it increases $\phi_2$ but decreases $\phi_1$ in cloudy updrafts. As a result, $C_{\phi_1,\phi_2}$ becomes more and more negative as the updrafts go up.

$\mu_{\phi_1}$ is large near cloud base (the upper right column) is because $q_{c,\text{ref}}$ is small, $\mu_{\phi_1}$ and $\mu_{\phi_2}$ are much smaller than $\mu_{\phi_2}$, indicating that reaction in the control case is slow and leads to very weak heterogeneities of $\phi_1$ and $\phi_2$ in cloudy updrafts. The upper left column plots the products of the correlation coefficients and coefficients of variation (i.e., the RHS terms of equation (11)). In the control case, $\gamma_{\text{seg}}$ is dominated by the RHS1 term (the covariance between $\phi_1$ and $q_c$) because the in-cloud heterogeneity of $\phi_1$ ($\mu_{\phi_1}$) is larger than that of $\phi_2$ ($\mu_{\phi_2}$).

As the relative abundances of $\phi_1$ and $\phi_2$ change in experiments in group 1, the reaction timescale and strength of in-cloud heterogeneities of the reactive tracers also change. The decompositions of $\gamma_{\text{seg}}$ for a $\phi_1$-dominant case (the case with $\phi_{2,\text{rel}}/\phi_{2,\text{rel}0} = 1/12$ and $\phi_1 \approx 400\phi_{2,\text{rel}}$) and a $\phi_2$-dominant case (the case with $\phi_{2,\text{rel}}/\phi_{2,\text{rel}0} = 12$ and $\phi_1 \approx 500\phi_{2,\text{rel}}$) are shown in rows 2 and 3 of Figure 4, respectively. Compared to the control case, the correlation coefficients are qualitatively similar in all three cases, but $\mu_{\phi_1}$ and $\mu_{\phi_2}$ can vary significantly. When $\phi_1$ is strongly dominant in cloudy updrafts, $\phi_2$ reacts quickly and thus has a short lifetime. The fast reaction leads to low values and strong in-cloud heterogeneities of $\phi_2$, giving the large value of $\mu_{\phi_2}$ (blue line in the right column of row 2), even though its updraft mean value is small. As a result, $\gamma_{\text{seg}}$ is dominated by the covariance term between $\phi_2$ and $q_c$ (RHS2 term, blue line in the left column of row 2). When $\phi_2$ is strongly dominant in cloudy updrafts, based on the same argument, $\gamma_{\text{seg}}$ is dominated by the covariance term between $\phi_1$ and $q_c$ (RHS1 term, red line in the left column of row 3).

We can define a Damköhler number ($D_{\phi}$) [e.g., Molemaker and Vilà-Guerau de Arellano, 1998; Krol et al., 2000; Schumann, 1989] as the ratio of the in-cloud residence time of air parcels in shallow convection ($\tau_{\text{con}}$) to the reaction timescale ($\tau_{\phi_1}$ and $\tau_{\phi_2}$) to characterize the influences of convection on the aqueous reaction,

$$
D_{\phi} = \frac{\tau_{\text{con}}}{\tau_{\phi_1,2}}.
$$
$D_a$ being far smaller than 1 indicates that the heterogeneity of reactive tracers in cloudy updrafts is small, and the updraft mean is adequate for the calculation of reaction rate. $D_a$ being close to or greater than 1 indicates that the segregation of reactive tracers in cloudy updrafts is significant and may need to be taken into account.

$\tau_{con}$ can be estimated by dividing the total cloudy air mass by total inflow,

$$
\tau_{con} = \frac{\int_{z_{ct}}^{z_{cb}} \alpha p dz}{M(z_{cb}) + \int_{z_{ct}}^{z_{cb}} \epsilon M dz},
$$

(13)

Using $\epsilon_{qt}$ this gives $\tau_{con} = 370$ s. Alternatively, Neggers et al. [2002] calculated the eddy turnover time of individual clouds as the cloud depth is divided by the cloud-averaged maximum vertical velocity. They found that the BOMEX clouds with different cloud depths have a relatively constant eddy turnover time of about 400 s (see their Figure 4), close to $\tau_{con}$ estimated here by equation (13). Note that $\tau_{con}$ can be much smaller than the “life time of a cumulus cloud ($\sim 10^3$ s), because a cumulus cloud is continuously fed with updrafts.
from subcloud layer. The reaction timescale of $\phi_1$ in the cloud layer as a whole can be estimated as the total $\phi_1$ is divided by the total reaction rate in cloudy updrafts,

$$\tau_{\phi_1} = \frac{\int_{z_{ct}}^{z_{cb}} \rho \phi_1 u \, dz}{\int_{z_{ct}}^{z_{cb}} \rho R_1 \, dz}. \quad (14)$$

$\tau_{\phi_2}$ can be estimated in a similar way. The reaction timescale on a particular level may differ from the overall timescale estimated from equation (14). For the control case, this gives $\tau_{\phi_1} \approx 5 \times 10^3$ s and $\tau_{\phi_2} \approx 3 \times 10^3$ s.

To represent the overall segregation error in the cloud layer, we define $\Gamma_{\text{seg}}$ as the vertically averaged $\gamma_{\text{seg}}$ weighted by the product of the cloudy updraft fraction and density. $\Gamma_{\text{seg}}$ and the $D_a$ of reactive tracers for all cases in group 1 are summarized in Figure 5. From left to right, the reaction regime changes from $\phi_1$ dominant to $\phi_2$ dominant. Correspondingly, $D_{a,\phi_1}$ changes from $\sim 10^{-3}$ to $\sim 1$, and $D_{a,\phi_2}$ changes from $\sim 1$ to $\sim 10^{-3}$ (Figure 5b). $\Gamma_{\text{seg}}$ is dominated by the covariances between $q_c$ and the tracer with the smaller reaction timescale (larger $D_a$). Thus, $\Gamma_{\text{seg}}$ is positive to the left end and negative to the right end. In either direction, the absolute value of $\Gamma_{\text{seg}}$ increases as the larger $D_a$ value between the two reactive tracers increases. As the larger $D_a$ approaches and exceeds 1, which indicates that the reaction timescale is close to or faster than the in-cloud residence timescale, in-cloud heterogeneities have greater impacts on the aqueous reaction, but errors are only about 10% when $D_a \approx 1$. In the real atmosphere, in situations in which the SO$_2$ concentration dominates the H$_2$O$_2$ concentration, O$_3$ may take in charge and play a bigger role in the aqueous oxidation of SO$_2$, resulting in reduced segregation between SO$_2$ and oxidants in cloudy updrafts.
3.4. Errors Due To Entrainment/Detrainment Rates

The dependence of entrainment/detrainment rates ($\epsilon/d$) on tracers can lead to errors in the EDMF model. For $q_t$ and $h_y$, because they are so well correlated, their $\epsilon/d$ are almost identical [e.g., Siebesma et al., 2003]. However, $\epsilon_{\phi_1}$ and $\epsilon_{\phi_2}$ diagnosed from the LES results show sizable differences from $\epsilon_{q_t}$ for the control case (Figure 6a). Since $\epsilon$ and $d$ are constrained by the mass flux equation (equation (5), i.e., $\epsilon_{\phi_1} - d_{\phi_1} = \epsilon_{q_t} - d_{q_t}$), here we only focus on the discussion of $\epsilon$. Because the reaction is slow in the control case ($D_{a,\phi_1,2} \approx 0.1$), the surface-originated tracer $\phi_1$ has $\epsilon$ similar to but slightly smaller than $\epsilon$ of $q_t$. The intersection of $\phi_{2u}$ and $\phi_{2d}$ around 800 m (Figure 2b) leads to the unrealistic oscillation and negative values of $\epsilon_{\phi_2}$ around that height. The tracer dependence on $\epsilon$ is largely due to the aqueous reaction. The actual detrained (entrained) air seldom has the cloudy updraft mean (environmental mean) properties [Romps, 2010; Dawe and Austin, 2011; Nie and Kuang, 2012b]. Because of the aqueous reaction, the differences between $\phi_{1,2}$ in detrained cloudy updrafts and their mean values in the cloudy updrafts are different from those of $q_t$. Thus, detraining (entraining) the same amount of cloudy (environmental) air leads to different fractional changes of the environmental (bulk plume) $\phi_{1,2}$ and $q_t$.

We estimate the errors of $R$ due to the tracer dependence of $\epsilon$ in the bulk plume model as follows. The bulk plume (equations (5)–(6)) starts at cloud base with $\phi_{1,2}$ and $\phi_{2u}$, diagnosed from LES. After integrating upward over each level, we calculate $\gamma_{seg}$ on that level from the LES results with equation (11) and use it to correct $R_v$. With the errors due to in-cloud heterogeneities fixed, what is left of the errors of $R_v$ is only due to the errors in the cloudy updrafts mean tracer values caused by the inaccurate $\epsilon/d$. The bulk plume model is integrated to the cloud top. The relative differences between the resulting $R_v$ and the LES $R_v$ are vertically averaged with the weighting factor of $a$ and density, giving an estimation of entrainment error ($\Gamma_{\text{entr}}$, with units of percent). Because $\phi_{2u}$ and $\phi_{2d}$ are very close to each other (Figure 2b), the differences between $\epsilon_{\phi_1}$ and $\epsilon_{\phi_2}$ have little
effect on the calculation of $\phi_2$. Analyses indicate that $\Gamma_{\text{ent}}$ is dominated by the differences between $e_{\phi_1}$ and $e_{q_t}$; therefore, our discussions hereafter focus on $\phi_1$ and $e_{\phi_1}$.

It is expected that $\Gamma_{\text{ent}}$ is also related to $D_a$. As long as the reaction timescale is large compared to the in-cloud residence timescale ($D_a \ll 1$), reactive tracers behave similarly to conservative tracers and $\Gamma_{\text{ent}}$ should be small. When the reaction timescale is close to or smaller than the in-cloud residence timescale, the aqueous reaction will have larger effects on $e$, leading to larger $\Gamma_{\text{ent}}$. The cases in group 2, in which we vary $k$ from $10^{-4}$ to $10^{-1}$, demonstrate the above argument. Figure 6b shows the $e_{\phi_1}$ for all cases in group 2. As $k$ increases, $e_{\phi_1}$ deviates farther away from $e_{q_t}$ to more negative values. Figure 7 shows $\Gamma_{\text{ent}}$ and $D_a$ of the group 2 cases as a function of $k$. As $k$ increases from $10^{-4}$ to $10^{-1}$, $D_a,\phi_1$ increases from $\sim 10^{-2}$ to $\sim 10^{-1}$ and $D_a,\phi_2$ from $\sim 10^{-2}$ to $\sim 1$. Consistently, as $D_a$ increases and approaches 1, the absolute value of $\Gamma_{\text{ent}}$ starts to increase sharply (Figure 7a). $\Gamma_{\text{ent}}$ is always negative because $e_{\phi_1}$ is always smaller than $e_{q_t}$ due to the aqueous reaction.

The analyses in sections 3.3 and 3.4 show that for most of the cases examined, the aqueous reaction can be viewed as slow ($D_a \ll 1$) compared to convective timescale. Thus, errors in the aqueous reaction due to segregation and the dependence of entrainment/detrainment rates on tracers are small. The EDMF model with diagnosed parameters from $q_t$ reproduces the transport and reactions of $\phi_1$ and $\phi_2$ quite well.

### 3.5. Evaluating the Operator-Splitting Error in CTMs

In this subsection, we evaluate the error due to operator splitting that is used in many CTMs. This is done by running the EDMF model but with the transport and aqueous reaction calculated separately over a typical CTM time step, as introduced in section 2.3.

Figure 8 summarizes the mean tracer concentrations (vertically averaged from the surface to the cloud top level) and mean aqueous reaction rate (vertically averaged from the cloud base to the cloud top level) in all the cases in the two groups. We first examine the LES results in group 1 (Figures 8a–8c), in which the relative ratio between $\phi_1$ and $\phi_2$ decreases moving from left to right on the $x$ axes. The dependence of $\phi_1$ and $\phi_2$ on...
the relative abundance of $\phi_1$ and $\phi_2$ ($x$ axes) is consistent with the experiment designs (note that the $y$ axes in Figures 8a and 8b are logarithmic). Figure 8c shows that the LES $R$ peaks when $\phi_1$ and $\phi_2$ are comparable in cloudy updrafts. The cases in group 2 (Figures 8d–8f) show that as $k$ increases, both $\phi_1$ and $\phi_2$ decrease, while $R$ increases.

The EDMF model results (red markers in Figure 8) match the LES results quite well for the three variables in all the cases. However, if the transport and aqueous reaction in the EDMF model are treated as separated operators as is done in many CTMs over $\Delta T_{\text{CTM}}$ (30 min in the calculation shown in Figure 8), the results (blue markers) show significant error. To provide a quantitative estimation of the errors, Figure 9 shows the normalized root-mean-square errors (NRMSEs) of $\phi_1$, $\phi_2$, and $R$ for all cases in the two EDMF model settings. The open markers indicate that the mean is underestimated by simple models, while the solid markers indicate that the mean is overestimated. Consistent with previous analysis, when $\phi_2$ becomes dominant ($D_{\phi_2}$ approaches 1), the NRMSE of $\phi_1$ increases (Figure 9a). The opposite holds when $\phi_1$ becomes dominant (Figure 9b).

For the second group of experiments (Figures 9d–9f), as $k$ increases, $D_{\phi_1}$ and $D_{\phi_2}$ approach 1, consistent with the increases of the NRMSEs. In all the cases, the error in the EDMF model is much greater if the transport and aqueous reaction are treated as separated operators than if they are calculated simultaneously.
Figure 9. The NRMSE of (a and d) $\bar{\phi}_1$, (b and e) $\bar{\phi}_2$, and (c and f) $\bar{R}$ of the results of the EDMF model (red) and the EDMF model with operators splitting (blue). Solid (open) marker indicates that the vertical averaged variables are overestimated (underestimated) by the simple model compared to the LES results. Figures 9a–9c are for the cases in group 1, and Figures 9d–9f are for the cases in group 2.

Figure 10. The control case NRMSE of $\bar{R}$ in the EDMF model with operators splitting as functions of $\Delta T_{CTM}$. The dashed line indicates NRMSE of $\bar{R}$ in the EDMF model with tracer transport and aqueous reactions calculated simultaneously.
Figure 11. The comparison between the LES and EDMF model in the transient case with $k = 10^{-3}$. (a–c) The time evolution of $\phi_1$, $\phi_2$, and $R$ of the LES results, respectively. (d and e) Differences of $\phi_1$ and $\phi_2$ between the EDMF model and the LES results, respectively. (f) The time evolution of $R$ of the EDMF model results (top) and the vertically averaged time series of $R$ of the EDMF model (red line) and LES results (black line) (bottom).

The errors due to operator splitting decreases as $\Delta T_{\text{CTM}}$ decreases (Figure 10, taking the control case as an example). However, even if $\Delta T_{\text{CTM}}$ decreases to 4 s, the same of the sub-CTM time step, operator splitting still leads to additional errors.

Although here we evaluate the errors due to the operator splitting in CTMs using the EDMF model, this error is independent of the EDMF model and exists in other mass flux-based convective parameterizations. On the other hand, a mass flux-based convective parameterization can reduce this error by calculating tracer transport and aqueous reactions in updrafts simultaneously [e.g., Berg et al., 2015].

3.6. Chemical Transient States

Although the above analyses are in chemical steady states, the EDMF model with diagnosed parameters also works well in transient states. In the following three transient cases ($k = 0, 10^{-3}, 10^{-1}$), the BOMEX case is initialized from hour 0 and runs for 6 h. The initial conditions of chemical tracers are $\phi_1$ being zero and $\phi_2$ being the reference value.

Figures 11a–11c show the LES-simulated evolution of tracer profiles and reaction rate of the $k = 10^{-3}$ case. As time progresses, $\phi_1$ builds up in the subcloud layer and is transported upward by convective updrafts. The aqueous reaction leads to the decrease of $\phi_2$ in the cloudy layer, and the $\phi_2$-depleted air is entrained into the subcloud layer and decreases $\phi_2$ there. $R$ becomes nonnegligible at about hour 0.5 and continues to grow, due to the development of shallow cumuli and the building up of $\phi_1$. During the thermodynamical steady period (hour 3 to hour 6), there is considerable variability of cloud fraction, reflected as the variation of $R$. This internal variability, however, can be reduced by increasing the LES domain size or averaging over an ensemble of simulations.
Figure 12. The hour 6 profiles of (a) \( \phi_1 \) of the \( k = 0 \) case; (b) \( \phi_1 \), (c) \( \phi_2 \), and (d) \( R \) of the \( k = 10^{-1} \) case. The red solid lines are the LES results, and the blue circles are the EDMF model results.

We run the EDMF model from hour 3 to hour 6, with the same entrainment/detrainment and the same eddy diffusivity parameters as the ones in previous subsections. The initial profiles of the reactive tracers are taken from the LES profiles at hour 3. The differences of \( \phi_1 \) and \( \phi_2 \) between the EDMF model and the LES results (Figures 11d and 11e) are small. \( R \) in the EDMF results shows smoother variation in time than it does in the LES results (color contour in Figure 11f). The comparison of vertically averaged \( R \) between the EDMF model and the LES (Figure 11f) shows that the EDMF model captures the LES results well. Figure 12 shows the comparison of the hour 6 profiles from the LES and the EDMF model (which also starts from hour 3) for the \( k = 0 \) and \( k = 10^{-1} \) cases. Without aqueous reaction (\( k = 0 \)), more \( \phi_1 \) is transported into cloudy layer (Figure 12a). With strong aqueous reaction (\( k = 10^{-1} \)), significant amounts of \( \phi_1 \) are only found in the subcloud layer (Figure 12b), since \( \phi_1 \) in cloudy updrafts quickly reacts near the cloud base (Figure 12d). In both cases, the EDMF model reasonably reproduces the LES results.

4. Conclusions and Discussions

The goal of this study is to improve the representation of aqueous phase reactions in shallow cumuli in global models. An LES with an idealized chemical reaction mimicking the aqueous oxidation of surface-originated \( \text{SO}_2 \) by \( \text{H}_2\text{O}_2 \) is used to guide simple models. We show that the EDMF approach with a bulk plume model is a promising solution. When entrainment/detrainment rates and eddy diffusivity are diagnosed using a conservative thermodynamic tracer (e.g., \( q_t \)), the EDMF model represents the transport and aqueous reactions of reactive tracers quite well over a wide range of parameters. The eddy diffusion component of the EDMF model is sufficient for parameterizing surface-originated chemical tracers, while it may neglect the tracer transport in the cloud shells for non-surface-originated tracers. The bulk plume component of the EDMF approach has two sources of errors: neglecting the heterogeneities within cloudy updrafts leads to a segregation error between reactive tracers and cloud water and the use of entrainment/detrainment parameters derived from \( q_t \) on reactive tracers leads to an entrainment error. Both of these errors are related to the reaction timescale. When the reaction is slow compared to the in-cloud residence time of air parcels, the reactive tracers behave like conservative tracers, so that the EDMF model that represents the conservative thermodynamic tracers well can also represent the reactive tracers well. When the reaction timescale approaches the in-cloud residence time of air parcels, in-cloud heterogeneity increases and the entrainment/detrainment rates of reactive tracers further deviate from those derived using conserved variables, resulting in greater errors.
The errors due to operator splitting are estimated by running the EDMF model in a CTM-like configuration where the tracer transport and aqueous reactions are calculated separately over a time step representative of CTMs, and the aqueous reaction calculations use horizontal mean (rather than updraft) tracer concentrations. The error due to operator splitting can be significant (>50% for all cases examined here with a CTM time step of 30 min), especially when the reaction is fast compared to the in-cloud residence time. The error decreases as the CTM time step decreases but remains larger than that of the case with tracer transport and aqueous reactions calculated simultaneously in the cloudy updrafts.

In this study, the parameters for the EDMF model are diagnosed from a conserved thermodynamical tracer. In GCMs, the uncertainties in these parameters, and therefore the parameterized convection, are still the leading source of errors for the representation of atmospheric chemistry. However, these uncertainties may be reduced by diagnosing convective parameters from the resolved convection of a cloud-resolving model inside each GCM column, a method known as the super-parameterized GCMs [Grabowski, 2001; Khairstoutinov and Randall, 2001], Gustafson et al. [2008] and Wang et al. [2011] have already adopted this approach and applied it in aerosol-climate simulations. In this study, we lend support to theirs, provide an evaluation of the approach in an idealized setting, and analyze the sources of errors and their dependence on chemical reaction regimes.

Although a bulk plume model is used in the EDMF model in this study, many convection parameterizations use multiple plumes/parcels to represent cloudy updrafts [e.g., Berg and Stull, 2005; NIE and Kuang, 2012a; Sušelj et al., 2013]. A multiple plume/parcel representation allows heterogeneities within cloudy updrafts, which can improve the representation of nonlinear microphysical processes [e.g., Krueger et al., 1997; NIE and Kuang, 2012b; Tölle and Krueger, 2014]. It can also potentially benefit the aqueous reactions by, for example, accounting for the segregation between reactive tracers in cloudy updrafts and having different entrainment/detrainment rates for each plume.

The current work focuses on the a nonprecipitating shallow cumulus convection with an idealized aqueous reaction. Future work is needed to include more realistic chemistry, additional complexities in convection (e.g., precipitation, downdrafts, and convective organization), and their possible interactions (aerosol-cloud interaction) [e.g., Berner et al., 2013; Wyant et al., 2015; Berg et al., 2015].

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