

The Impact of Chemistry on Flux Estimates in the Convective Boundary Layer

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ABSTRACT

Different higher-order flux closures are compared for two chemistry cases using a large eddy simulation (LES) model for the convective atmospheric boundary layer. Both a simple chemistry case and a photochemistry case more representative for atmospheric chemistry are studied. The turbulent vertical fluxes are decomposed into two parts, one independent and the other dependent of chemical higher-order moments. The LES results are used to determine the contribution of chemical higher-order moments to the flux for the higher-order closures. It is found that this contribution is sensitive to the closure assumptions. However, it is expected that the differences between different closures will be small in realistic applications. Therefore it is concluded that first-order closure suffices for large-scale atmospheric chemistry models to model the turbulent vertical flux of reactive species in the atmospheric boundary layer.

1. Introduction

The fluxes of nonreacting scalars near the surface can generally be modeled using local K theory. Away from the surface, in the bulk of the convective atmospheric boundary layer (CABL), local transport does not suffice to model scalar fluxes and nonlocal transport effects have to be taken into account (e.g., Holtslag and Moeng 1991). For chemically reacting species the flux–gradient relationships near the surface are modified due to chemical reactions. In the bulk of the CABL the nonlocal flux contribution in nonlocal first-order closures is also modified due to chemical reactions (Petersen and Holtslag 1999). In this paper we study the chemical influence on flux–gradient relationships near the surface using the large eddy simulation (LES) technique, which has not been used for this specific purpose before.

The flux budget of reactive species is sensitive to chemistry in two major ways. First, the flux budget is dependent on the profile of mean concentrations (which is affected by the chemistry through the concentration budget). Second, the flux budget (and budgets of all other higher-order moments that contain species concentrations) includes higher-order moment terms related to the chemistry. In this study we present an exact decomposition of the flux budget and we examine the chemical higher-order moment contribution to the flux. The contribution of the higher-order moments to the flux

leads to a modification of the flux–gradient relationships near the surface.

When applied to higher-order flux closures the decomposition leads to different outcomes for different closure assumptions. The typical approach that has been followed to determine the chemical higher-moment contribution is by way of second-order closure modeling (e.g., Fitzjarrald and Lenschow 1983). We will compare versions of a formulation that is along this line (Verver et al. 1997) with versions of a new formulation, a mass-flux closure, developed in this paper (based on Petersen et al. 1999; de Roode et al. 2000). In order to do this we have defined a simple chemistry case for which the modification of the flux–gradient relationship near the surface due to chemistry is significant. We will also assess the significance of the fundamental findings for realistic applications in atmospheric chemistry modeling. For that purpose we study a second case that is more representative for atmospheric chemistry.

The structure of this paper is as follows. In section 2 we introduce the flux budget equation and its decomposition. Sections 3 and 4 give the second-order closure and mass-flux closure formulations, respectively. The results of the intercomparison are given for both cases in section 5. Finally, the results are summarized and discussed in section 6.

2. Theory

The flux budget equation for a chemical species s_i , assuming horizontal homogeneity and $\overline{w} = 0$, reads

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