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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Study of the diurnal variability of atmospheric chemistry with respect to boundary layer dynamics during DOMINO" *by* B. J. H. van Stratum et al.

**B. J. H. van Stratum et al.**

bart.vanstratum@wur.nl

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We thank Referee #1 for his/her careful assessment of the manuscript. The points raised by the referee have been addressed below.

**General comments**

The reviewer raised two interesting questions concerning physical assumptions of mixed-layer theory: 1) the difference between surface layer and mixed-layer model results and 2) the reactivity efficiency due to the segregation of reactive species.



First, the height of the measurements was indeed not mentioned in the manuscript, which has now been corrected. As correctly guessed by the reviewer, all measurements were made near the surface (10 - 12 m a.g.l.). The differences between surface layer and mixed-layer averaged values have before been addressed by Vilá-Guerau de Arellano et al. (2011) by comparing the results of a mixed-layer model with identical numerical experiments carried out in large-eddy simulation (LES). Their findings (for isoprene and MVK) were that surface-emitted species indeed have a higher mixing-ratio near the surface, but that the tendencies and mixing-ratios in the mixed-layer model show a satisfactory agreement with both measurements and LES. Furthermore, the observed differences between surface and mixed-layer averaged values are well within the uncertainty of the measurements (see Fig. 2 and 3 of their article). We have added a short discussion on this topic to the case description in section 3.

The segregation of species, which might lead to a modification of the reaction rate, has recently been addressed by Ouwersloot et al. (2011) by explicitly calculating the influence of segregation in LES. Their results indicate that there is only a small influence of segregation on the reaction rates, and in their conclusions write: *"Consequently, the chemical reaction rates remain almost equal, which explains the satisfactory performance of mixed layer models that assume instantaneous mixing for atmospheric chemistry in the planetary boundary layer during diurnal convective conditions"*. Dlugi et al. (2010) found a similar order of magnitude of the intensity of segregation (around 10%) by measuring the covariance of isoprene and hydroxyl above a forest. These findings are further supported by the the agreements between LES and mixed-layer model results in Vilá-Guerau de Arellano et al. (2011). We have extended section 2.2 ("Representation of chemistry") on this subject by shortly introducing the work of Dlugi et al., Ouwersloot et al. and Vilá-Guerau de Arellano et al., and previous work by Vinuesa et al. (2003) on including the intensity of segregation in a mixed-layer framework.

### Specific and technical comments

All other specific and technical corrections have been applied as proposed by the reviewer.

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