**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "In-canopy gas-phase chemistry during CABINEX 2009: sensitivity of a 1-D canopy model to vertical mixing and isoprene chemistry" *by* A. M. Bryan et al.

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In the following response, the line numbers refer to the lines in the revised manuscript. References to figures uploaded in the response are denoted Fig. R1, Fig. R2, etc., to distinguish from references to figures in the main text (Fig. 1, Fig. 2, etc.) and the supplementary material (Fig. S1, Fig. S2, etc.)

1) The main issue that really deserves more attention in this ms is the role of surface deposition in potentially explaining some of the discrepancies between the simulated and observed oxidation products that are now partly attributed to potential issues on the other processes.

We have made several substantial modifications to the manuscript to discuss the role of deposition. We address the reviewer's specific comments regarding the treatment of deposition in CACHE. Please see comments 3, 6, 7, 13, and 14 below for detailed responses.

2) Line 234: "Measured NO2, HCHO, and MACR concentrations are used to tune advection rates for the model scenario that incorporates both nudged turbulence and RACM-MIM chemistry". Reading through your section on how you treated the role of advection I was wondering why you did not nudge (you state that you are nudging the models turbulence so you are familiar with such rather technical numerical simulation features) the model simulated boundary concentrations using the observed concentrations of some of the long-lived compounds such as NOx, CO and O3? This would secure your model to simulate the observed boundary layer concentrations and then let the canopy exchange model calculate how this "translates' into the canopy exchange fluxes and concentrations. I have used this approach in the analysis of canopy exchange processes for different sites and this seems to secure a optimal way to ensure a fair evaluation of these models for those compounds with relative short exchanges timescales compared to that of advection.

For the purposes of elucidating the relative sensitivities of biogenic chemistry to the representation of mixing and isoprene degradation in a model, we minimize the number of observational constraints in this analysis to develop as prognostic a model as possible. While driving some model parameters with observations can be useful for identifying sources of bias and uncertainty, it can also yield misleading results, particularly with atmospheric composition since gases have a complex dependency on one another. As we show in our paper, NOx and O3 are particularly sensitive to the representation of mixing in the model; a fact that would not have been discovered had observations of these gases been used as input into the model. We agree that using observed trace gas concentrations to drive the model could improve our understanding of chemistry at the PROPHET site and we plan to test this approach in future model

simulations.

3) Section 2.3; reading over the section on the model set-up this is only addressing the issue on how the BVOC (and NO) emissions have been included for this specific analysis but there is no information at all about how you have treated dry deposition and potentially relevant foliage NOx emissions associated with nitrate photolysis. I am aware that the focus is on BVOC cycling and the role of turbulence and chemistry but 1) because of the role of O3, NOx, oxidants (peroxides) but also oxygenated species in canopy photochemistry and exchanges and 2) recent findings that the dry deposition of some of those components might be quite different from what we always assumed (and how it is represented in CACHE?) (oxygenated species and VOC products; Karl et al., 2004 & 2011, peroxides; Ganzeveld et al., 2006), it is relevant to discuss how this process has been considered in your study. How is for example stomatal and non-stomatal uptake being considered in the model? A change in the representation of turbulent exchanges as you present in your study might have large (if VOC product and peroxide removal is âLijturbulent limited) or small (using the "traditional" Wesely approach removal rates) consequences on the efficiency of removal of some of these compounds and their simulated concentrations.

A detailed description of the treatment of dry deposition has been added to model description (lines 271–298) along with a new figure showing simulated deposition velocities (Fig. 1). The reactivity factors (f0) for MACR and HCHO were adjusted from the original Wesely (1989) values (f0 = 0) to the revised values (f0 = 1) proposed by Karl et al. (2010) in the original version of this manuscript, leading to deposition velocities within the expectations of Karl et al. (vd,MACR < 2.4 cm s-1, Fig. 1). This has been noted in Sect. 2.2.4 (lines 292–296) and in the summary and conclusions (lines 736–738). H2O2 deposition is insensitive to enhanced mixing (Fig. R1a) and fluxes resemble the underestimations observed by Ganzeveld et al. (2006) (Fig. R1b). Unfortunately, H2O2 was not measured during the CABINEX 2009 field campaign, and the observational data presented by Ganzeveld et al. (2006) takes place in a different

ecosystem (coniferous vs. mixed) with a substantially larger ecosystem-level LAI (5.3 m2 m-2 vs. 3.8 m2 m-2); therefore, it is unclear how strongly the stomatal resistance for H2O2 must be adjusted to produce realistic H2O2 deposition. Instead, we discuss the potential caveats of using Wesely (1989) presented by Ganzeveld et al. (2006) and its implications on peroxide deposition efficiency in the revised manuscript (lines 296–298, 740–742). Foliage NO2 emission is not considered in this study (see new text on lines 269–270).

4) Lines 330-334: "Because the BASE model parameterization typically classifies stable conditions when PAR decreases at the end of the day, the modeled KH abruptly decreases at the onset of sunset resulting in an end-of-day decrease in mixing that is nearly two hours earlier than observed. We note that CACHE does not account for heat storage within the canopy biomass and this is also likely contributing to the early onset of stability in the model at the end of the day". This issue of the model makes me wonder how well the model simulates the in-canopy energy balance and temperatures. You would expect that during the afternoon the soil (and understorey) warm up and that in the late afternoon, early evening, the lower part of the canopy and especially the soil is warmer compared to the crown-layer that would enhance the mixing. It would be interesting to see, also since CACHE calculates these feature explicitly, how the simulated lower-canopy and soil temperatures compare to observations for the BASE and MIX case. Because of the important role of in-canopy stability on mixing efficiency, the changes in temperatures due a change in mixing effect mixing conditions consequently introducing ("a numerical") feedback mechanism.

We added a discussion of the model's simulation of in-canopy temperatures (lines 373–376) with reference to a new figure comparing the observed temperatures with the BASE and MIX simulations at three measurement heights (34 m, 20.4 m, and 6 m) (Fig. 3). The good model-measurement agreement illustrates how well the model simulates the diurnal temperature cycle, as well as how enhanced mixing improves in-canopy temperatures. We note that we did not attempt to introduce heat advection

nor the change in air masses, hence the obvious discrepancies prior to the frontal passage (∼7 EST) on day 1. Modeled soil temperatures are warmer than the canopy at night, as the reviewer expects, which increases in-canopy mixing from ∼0.01 m2s-1 during the day to ∼0.1 m2s-1 at night (Fig. R2), although we note the relatively small values of KH. We are unable to evaluate modeled soil temperatures because of a lack of measurements during CABINEX 2009. We have added text to explain this below-canopy mixing and the limitations due to the lack of measurements in this region (lines 442–445).

5) Line 346; "This is an artifact of the use of two different equations to construct the in- and above-canopy wind profiles and turbulence schemes, which creates a discontinuity at the forest-atmosphere interface and prevents BVOC transport out of the canopy sub-layer in the model". This apparently really addresses a potential model flaw that is now fixed having established the important role of turbulence in simulations of BVOC exchanges.

We reiterate this comment in the conclusions to emphasize the importance of this finding for future 1D canopy modeling efforts (lines 696–698).

6) Line 355: "For the longer-lived species (formaldehyde, MACR+MVK, and acetalde-hyde), concentrations are decreased and gradients are weakened by the enhanced mixing". The analysis of the impact of a changed mixing of these component is especially dependent on the representation of their sinks including OH/O3 oxidation but also potentially the removal by dry deposition or even some biogenic source (existence of compensation point for formaldehyde).

Karl et al. (2010) note the possibility that oxidized VOCâĂŤMACR+MVK in particu-larâĂŤmay deposit as efficiently as O3, and suggest that models employing the We-sely (1989) deposition algorithm set the reactivity factor (f0) to one. This change was implemented for the HCHO and MACR RACM species in the original version of this manuscript, yet enhanced mixing still leads to uniform vertical concentrations, which

C6379

may argue for a compensation point as the reviewer suggests. We acknowledge this possibility in the revised manuscript on lines 398–401.

7) Line 374; This suggests that in-canopy O3 concentrations are more influenced by local chemistry than regional transport at the canopy-scale, as observed, e.g., by Wolfe et al. (2011)". This stresses the weakness of this analysis. Misrepresentation of the in-canopy O3 mixing ratios is attributed to chemistry whereas another quite important explanation might be the role of in-canopy sinks such as understorey vegetation- or soil deposition that would be anticipated to be rather efficient for expected organic soils at this site.

We agree with the reviewer that a discussion of deposition is greatly needed here and have substantially revised Sect. 3.2 (lines 413–447). We have evaluated the changes in ozone concentrations due to advection, chemical production/loss, deposition, and mixing, and as the reviewer notes, have found that deposition plays an important role in controlling the concentrations under clean-air conditions. We calculate maximum deposition rates of O3 on the order of 1–10 ppbv min-1, exceeding the loss rate to chemistry by an order of magnitude. Modeled deposition fluxes compare well with observed fluxes by Hogg et al. (2007). As noted in the manuscript, the change in O3 deposition velocity from BASE to MIX is small (<0.02%), yet the diurnal cycle is removed upon changing to MIX, indicating that the O3 deposition fluxes are not sensitive to mixing in our model (lines 439–442).

8) Line 383: "or a missing NO2 source in the model". What would be a nocturnal NO2 source besides the NO+O3 reaction?

We note that our wind-direction-dependent advection scheme prescribes advection rates for a broad range of wind directions. It is also entirely possible that NO2 advection is sensitive to other factors in addition to wind direction. Therefore, we view advection as the most likely missing source of nocturnal NO2 in the model. Secondly, downward mixing of NO2 from aloft associated with entrainment from the residual layer could

C6380

explain the missing source if such downward mixing is inhibited in the model. We note these considerations in the revised manuscript in order to clarify that the missing source may not be strictly chemically based (line 454–455).

9) Having checked in detail figure 3 it is obvious that its layout should be changed. It took me a long time to understand the legend since these are plotted on top of the figures which suggests that these legend names are to be connected to the figures found under these names. Could you put the legends close to each other on the right hand side of the figure and include again the explanation of the colors fitting to the specific figures in the figure caption?

We have relocated the legends in Figs. 5, 6, and 8 (formerly Figs. 3, 4, and 6) according to the reviewer's suggestion, though moved them inside the figure rather than outside the figure to minimize whitespace. The figure caption for Fig. 5 has been revised to include a complete description of the model scenarios listed in the legendâĂŤFigs. 6 and 8 refer the reader back to Fig. 5 for this complete description.

10) The reviewer raises several important points in this comment:

a) Line 401- ; and the modeled diurnal pattern is prevalent in many modeling studies (e.g., Sillman et al., 2002; Forkel et al., 2006; Barkley et al., 2011), which attribute the end-of-the-day increase to subsidence associated with the compression of the PBL". Are these your own wordings or those of the references you mention here?? I don't think that you really have a compression of the PBL in the evening. The forcing of the PBL growth will stop and you will actually get the onset of the formation of an inversion layer below the residual layer with a decrease in the sensible heat flux... We agree with the reviewer's argument and have revised the text of the cited studies (lines 476–477). CACHE simulates a stable nocturnal boundary layer below the residual layer in which $\partial\theta/\partial z$ is positive, resulting in highly reduced turbulence (Fig. R2) and VOC accumulations in the canopy layer (lines 477–493).

b) ...but the decrease in mixing might be not that large since you might have enhanced

C6381

mixing conditions inside the canopy (warmer soil compared to crown-layer); in such situations I can imagine that the reference height of the observations that you use for the evaluation becomes very critical. As discussed in comment (4), we do see enhanced mixing within the canopy at night, although the magnitude is small and not sufficient to mix VOC out of the canopy. However, we acknowledge that we do not have below canopy turbulence observations to drive the model in the lower canopy, and may therefore be underestimating below-canopy turbulence (lines 485–487).

c) But you also wonder to what extent your model (and the other models) properly represents the temperature that really controls the VOC emissions in the late afternoon. You might not expect that global model system, e.g., used by Barkley et al., would realistically simulate these day-night transitions but you could analyze with your model how well it simulates the decrease in crown-layer temperature associated with long-wave cooling. As discussed in comment (4) and shown in the Fig. 3, canopy temperatures are well simulated by CACHE, especially in the MIX simulation, indicating that the temperatures used in the emission parameterization are realistic. In addition, this suggests that CACHE accurately captures long-wave cooling in the crown layer. We have added a discussion of the canopy temperatures (lines 371–376).

11) Line 413; "Our evaluation of the BASE and MIX turbulence schemes presented in Sect. 3.1 discusses several observed model measurement discrepancies in BASE-case KH that are corrected in the MIX scenario, including the two-hour offset between the modeled and measured diurnal cycle of KH". In a study on analysis of atmospheric chemistry observations over Guyana's tropical forest (Ganzeveld et al., Atmos. Chem. Phys., 8, 6223–6243, 2008) we discussed the problem on a misrepresentation of the early morning transition in mixing for chemical exchanges and the evaluation by comparison with the models. In that case it turned out that part of the problem is also the representation of the energy partitioning with incoming energy in the morning being used to evaporate canopy water resulting in a further temperature drop in the morning after sunrise further delaying the onset of mixing. To what extent are such features

C6382

also a potential explanation for some of the issues on turbulence in CACHE (recognizing the fact that Renate Forkel has also been working on the role of dew in chemical exchanges....)

We have revised the text to clarify our use of the term "two-hour offset," which is misleading upon re-examination of Fig. 2. The BASE model version captures the timing of the morning mixing onset fairly well, but predicts a decrease in mixing at sundown approximately two hours too early. We have revised this statement to reduce confusion (lines 487–490). Dew is only considered at the soil interface and not on leaf surfaces. Precipitation intercepted by the canopy is considered in the calculation of canopy temperatures, but rain does not occur during the simulation period chosen for this study. Considering that canopy temperatures are well simulated by CACHE, as noted in comment (4), we do not expect that evaporation of canopy water in the morning could explain the turbulence discrepancies.

12) Line 419-420 and paragraph; "While enhanced mixing improves the diurnal evolution of isoprene, modeled mixing ratios exceed observations on the second day by 1–3 ppbv, likely due to an underestimate of isoprene oxidation". This is an interesting finding that stresses the difference between your analysis and that by Wolfe et al. (2011) who conducted an analysis focusing on one midday event. You discuss the noted discrepancy between the observed and simulated isoprene in terms of a misrepresentation of nighttime chemistry. However, this might only be part of the explanation. It would be interesting to see the results with your model system on the oxidation products for the second day where I would expect them to be also enhanced associated with the downward mixing of those products partly consuming the OH not being available for isoprene oxidation (this was also discussed in the 2008 ACP paper). Those products (e.g., CH2O) can accumulate overnight in the residual layer due to the ongoing nighttime chemistry and a decoupling from the surface avoiding any destruction by surface deposition. It would be nice to see if this feature is also present in your model (we also found this feature in the model analysis by Barkley et al. 2011) further confirming the

importance of this boundary layer feature in chemical exchanges modeling.

Figure R3 shows simulated methacrolein (MACR) concentrations overlaid with concentration tendencies (e.g., the change in MACR due to mixing alone). MACR accumulates in the residual layer overnight, as expected. At sunrise on the second day, MACR concentrations increase in the canopy coincident with the positive concentration tendency due to mixing (solid contours), suggesting that downward transport of oxygenated VOC accumulated in the residual layer is captured by our model. However, MIX-simulated isoprene concentrations begin to overestimate observations at sundown on the first day—well before the morning downward transport of oxygenated VOC—leading to our statement that the lack of isoprene loss may be responsible for the overestimations. We agree with the reviewer that downward transport of oxygenated VOC could have some degree of influence on OH availability for isoprene oxidation, though this would not occur in our simulations until the early morning of the second day. We have added this discussion on lines 507–513.

Caption for Fig. R3: Simulated methacrolein (MACR) concentrations (color-filled contours) in ppbv overlaid with methacrolein concentration tendency ($\partial[MACR]/\partial t$) with respect to mixing (line contours) in ppbv min-1. Solid contours indicate positive tendency ($\partial[MACR]/\partial t \geq 0$ ppbv min-1); dotted contours indicate negative tendency ($\partial[MACR]/\partial t < 0$ ppbv min-1). The horizontal dotted lines represent the top and bottom of the crown layer.

13) Line 453: "measured-modeled comparisons improve above the canopy but not below the canopy, suggesting either that there is in-canopy production that the model does not capture"; is this not indicating the possible importance of the representation of dry deposition/the issue on the existence of a CH2O compensation point?

We agree with the reviewer's suggestion of a potential compensation point for formaldehyde and have updated our discussion to include it (lines 540–544). Our results show overestimates in in-canopy HCHO concentrations despite overestimating the deposi-

tion velocity. A compensation point could readily explain this observation.

14) Line 472: "Consequently, modeled concentrations of the MACR RACM-MIM surrogate overestimate measured MACR+MVK by a factor of three throughout the profile"; also this finding really urges for some explanation how the deposition of the products are treated in CACHE.

We added a comparison of deposition velocity in CACHE with observationally derived deposition velocities by Karl et al. (2010) and Misztal et al. (2011) for MACR+MVK (lines 565–570). Simulated deposition velocities compare well with the cited observations after adjusting the reactivity factor (f0) according to Karl et al. (2010), yet MACR still overestimates observations, indicating that deposition is an unlikely explanation for the these discrepancies.

15) Line 481: "(200 - 500 pptv)".

We corrected this typo (line 575).

16) Line 493: "At the PROPHET site, however, the correlation between MACR+MVK and isoprene is weak (r2 =0:03) as a result of highly variable MACR+MVK advection with respect to wind direction;". Here you attribute the low correlation between MACR+MVK and isoprene completely to advection. It would be interesting to see how much of the MACR+MVK during the second day can be attributed to the entrainment of residual air masses relative to the contribution by advection. Does your model include the specific process tendencies as a diagnostic tool to separate those two different contributions?

In accordance with the reviewer's suggestion, we have expanded a discussion of MACR+MVK advection and the role on MACR+MVK/isoprene ratios based on our results and prior studies (Apel et al., 2002) (lines 585–592) and include a supporting figure in the supplementary material (Fig. S4) on the role of wind direction. Our model does simulate a small amount of downward transport of MACR in the early morning

C6385

(08–09 LT) associated with entrainment from residual air masses aloft on the order of 10 ppbv/min (Fig. R3). However, the weak correlations evaluated in Fig. 9 are later in the day (11–17 LT) and not likely affected by the entrainment. Based on the relatively small contributions from the downward mixing only in the early morning, we expect that the weak correlation is due to the differences in wind-direction dependent advection of isoprene oxidation products. We also incorporate the following correction in the revised manuscript (Fig. 9, lines 591 and 608): the square of the rank correlation coefficient ("Spearman's rho") is replaced with the square of the linear Pearson correlation coefficient.

17) Line 518: "Previously, other studies have attributed measured-modeled discrepancies to boundary layer dynamics, but our results suggest an important contribution from forest-canopy exchange". I would say it is the combination of both, during the daytime large-scale BL turbulent motions might control the exchange between the forest and the atmosphere (sweeps) whereas at nighttime the strong long-wave cooling triggers the formation of the inversion layer decoupling the residual layer from the surface. I am making this point since according to me both components need a high priority in improving chemistry simulations in a suite of 1-D to 3-D models.

We agree with the reviewer that the stable nocturnal boundary layer is an important mechanism for suppressing mixing and its accurate representation in models is key to understanding forest-atmosphere exchange. We have omitted the original statement and incorporated the boundary layer dynamics into our discussion of model-measurement discrepancies of BVOC (lines 615–616).

18) Line 557; "as does the explicit reaction of ISOP+ISOP". I don't get this one; could you explain in more detail what you mean with this?

RACM (Stockwell et al. 1997) does not treat the self-reaction ISOP + ISOP explicitly. RACM-MIM, however, does include the self-reaction, leading to lower ISOP concentrations, and thus much lower [HO2*]. We have rephrased the statement for clarity (lines

C6386

652–654).

19) Line 730; better refer to the paper that presented the analysis on the peroxide exchanges; Ganzeveld, L., Valverde-Canossa, J., Moortgat, G., Steinbrecher, R., Evaluation of Peroxide Exchanges over a Coniferous Forest in a Single-Column Chemistry-Climate Model, Atmos. Environ., 40, S68-S80, 2006.

We replaced the previous reference with the one suggested by the reviewer (lines 851–853).

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C6375/2012/acpd-12-C6375-2012-supplement.pdf

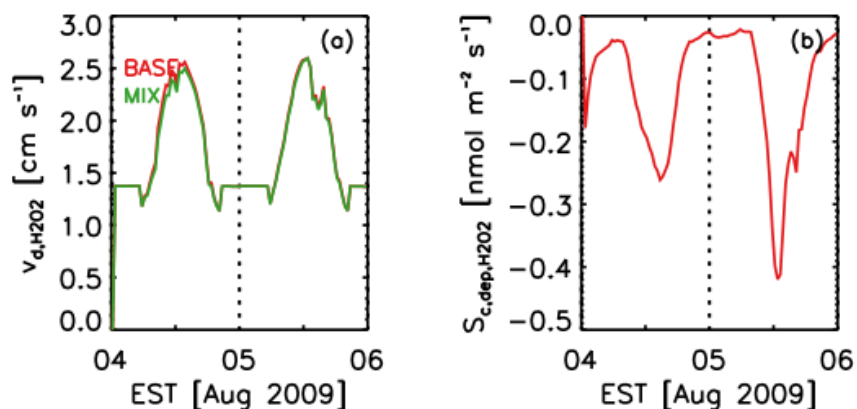Interactive comment on Atmos. Chem. Phys. Discuss., 12, 12801, 2012.

C6387

Fig. 1. (a) Canopy-integrated deposition velocity for the BASE and MIX simulations and (b) deposition flux for H2O2âĂŤcompare with Ganzeveld et al. (2006, Fig. 1a)
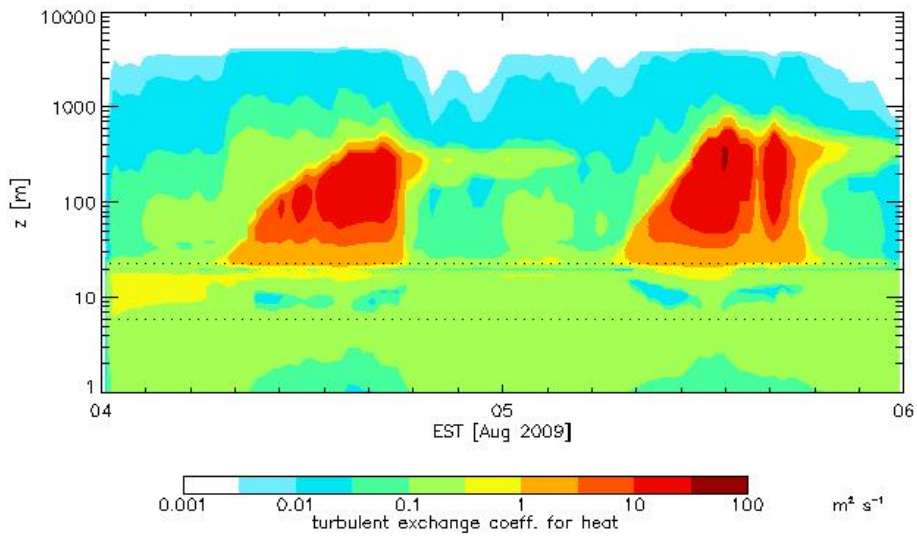
Fig. 2. Time evolution of the vertical profile of BASE-simulated KH. The dotted lines represent the lower and upper limits of canopy foliage
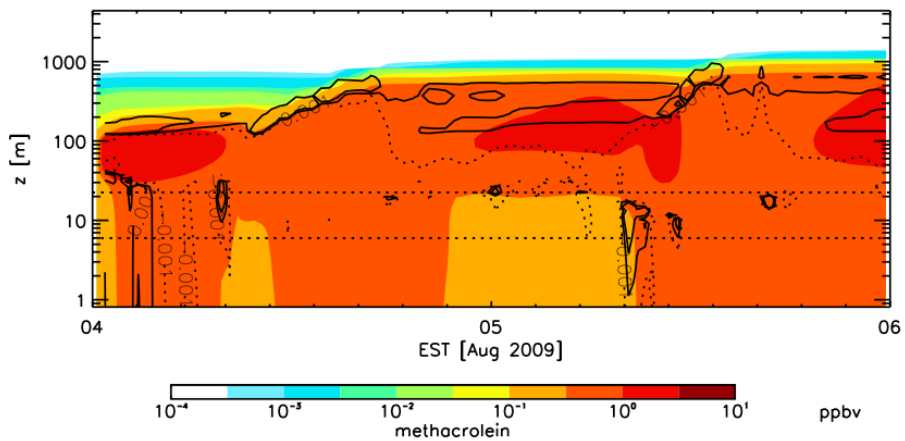
Fig. 3. Simulated methacrolein (MACR) concentrations in ppbv overlaid with methacrolein concentration tendency (∂[MACR]/∂t) with respect to mixing in ppbv min-1. See full caption in text.