Reply to comments on "Boreal forest BVOCs exchange: emissions versus in-canopy sinks" by Anonymous Referee # 2

October 21, 2017

We really appreciate the reviewer's detailed and valuable comments which help to improve our manuscript and clarify our discussions. All the comments are replied below.

1. **Comment: Is this code being made publicly available to the scientific community? I see no mention of this.**

   Reply: We will attach the python code of calculating the Henry's law constants and reactivity factors which is not a part of SOSAA currently. The whole SOSAA code is available by contacting Michael Boy (michael.boy@helsinki.fi) or Zhou Putian (putian.zhou@helsinki.fi). A two-month visit to the group of Dr. Boy is required to achieve the SOSAA model to ensure that the person is able to understand the basics of the code.

2. **Comment: 18L13 and Fig 5a, it seems from this that only 20% of emitted methanol makes it out of the canopy. This seems very low. Given that methanol is one of the largest BVOC fluxes to the atmosphere globally, your finding would seem to imply a much larger gross emission flux than is broadly recognized, with the vast majority never making it out of the canopy. It would be worth discussing this in more detail and comparing with other analyses/measurements that have addressed this point.**

   Reply: More discussion about methanol budget was added.

   P18, L14: "Hence their fluxes are bidirectional in the simulation (Figs. 4c-f)."

   →

   "Hence their fluxes are bidirectional in the simulation (Figs. 4c-f). The results indicate that a large portion of methanol molecules are deposited inside the canopy instead of being transported out of the canopy, which were also noticed by other studies. Karl et al. (2005) found methanol was deposited mostly in the lower canopy part during daytime and uptaken significantly inside the canopy at nighttime in a loblolly pine forest in July, 2003. Laffineur et al. (2012) even reported net daily negative methanol fluxes in a temperate mixed forest in summer during 2009 and 2010. At SMEAR II, Rantala et al. (2015) showed that from April to September during 2010 to 2013 the ratio between the cumulative deposition and the cumulative emission was slightly lower than 40%, which is about half of that in this study (80%). This discrepancy may result from the soil deposition explicitly calculated in this study, which is about 42% of the overall dry deposition sink of methanol. "

3. **Comment: Fig. 8, I don't see how to reconcile the data shown in Fig 8 with that shown in Fig 5. As an example, in Fig 5a we see that deposition is 5x more important than turbulent transport in removing methanol from the canopy airspace. In Fig 8e we would draw the opposite conclusion, that turbulent flux out of the canopy (blue line) is more important than deposition (purple line). Perhaps**

it's hard to visually integrate the area under the blue versus purple curves in 8e, but certainly the purple line integral is not 5x the blue line, and it appears to be less. The budget discussions need to be clarified so the reader fully understands what is being shown for the various figures.

Reply: In Fig. 8e methanol is transported out of the upper canopy layers. It can be transported either upward out of the canopy or downward into the lower canopy. In the lower part of the canopy, turbulent transport increases the methanol concentration as a source to compensate the deposition (-1.17 μg m^{-3} h^{-1}) onto soil surface. Therefore, turbulent transport acts as a sink term in the upper part of canopy and a source term in the lower part, which counteract each other. Therefore the overall effect of turbulent transport is -0.66 μg m^{-3} h^{-1} and the value for deposition is -2.77 μg m^{-3} h^{-1} which is about 4.2 times larger. This is consistent with the results shown in Fig. 5a.

4. **Comment: 5L14, some more information about the implementation of MEGAN within the model should be provided, as there have been different MEGAN versions, and there are different options for things such as treatment of the canopy, inclusion or not of a soil moisture effect, etc. Also the paper being cited (Guenther et al. 2006) only includes a description for isoprene whereas many more compounds are being simulated here.**

   Reply: Some texts were added to clarify the MEGAN module used in this study.

   P5, L13-15: "The BVOC emissions from the forest ecosystem are computed by MEGAN (Model of Emissions of Gases and Aerosols from Nature; Guenther et al., 2006)."

   →

   "The BVOC emissions from the forest ecosystem are computed by a modification version of MEGAN 2.04 (Model of Emissions of Gases and Aerosols from Nature; Guenther et al., 2006) which was described in details in Mogensen et al. (2015) and Zhou et al. (2017)."

   P11, L9: "The emissions of 15 organic compounds are included in current simulations, which are α-pinene, β-pinene, Δ3-carene, limonene, 1,8-cineole, OMT, β-caryophyllene, farnesene, OSQ, isoprene, MBO, methanol, acetaldehyde, acetone, formaldehyde. Their standard emission potentials (SEPs) for July, 2010 at SMEAR II ..."

   →

   "The emissions of 15 organic compounds (α-pinene, β-pinene, Δ3-carene, limonene, 1,8-cineole, OMT, β-caryophyllene, farnesene, OSQ, isoprene, MBO, methanol, acetaldehyde, acetone, formaldehyde) are computed in current MEGAN module according to the canopy structure described in Sec. 2.1. In this study only the emissions from the Scots pine are considered (Mogensen et al., 2015). The soil moisture is large enough during the whole month so that the activity factor for soil moisture is always equal to 1.0. The standard emission potentials (SEPs) of these 15 compounds for July, 2010 at SMEAR II ..." "

5. **Comment: 11L25, the wording here is confusing: "the SEP of methanol is estimated to be ~ 75 ng/m2/s by considering both emission and deposition processes . . .". I guess what is meant is that the 75 represents the gross emission flux (as derived from the net flux after accounting for deposition) since you are explicitly simulating deposition as a separate process. But from your wording it sounds like 75 represents the net flux, which wouldn't make sense. Please clarify language.**

   Reply: Yes, here 75 ng m^{-2} s^{-1} represents the emission flux. Rantala et al. (2015) applied an exchange algorithm including emission (E) and deposition (D) to parametrise the net flux of methanol (F):

$$F = E - D$$

Here E is dependent on methanol SEP and other meteorological conditions, while D has nothing to do with SEP. Then the SEP of methanol was calculated from measurement data (F and other meterological quantities) as 75 ng m^{-2} s^{-1} for July at SMEAR II, which was used in our study to calculate the methanol emissions. Text here was modified.

P11, L25-26: "The SEP of methanol is estimated to be $\sim$ 75 ng m^{-2} s^{-1} by considering both emission and deposition processes for July at SMEAR II in Rantala et al. (2015)."

→

"The SEP of methanol is set to $\sim$ 75 ng m^{-2} s^{-1} as suggested in Rantala et al. (2015)."

6. **Comment: 16L32, 'the observed large range in formaldehyde fluxes' . . . it is not clear why you would say this, as the range in Fig 4f only covers a total of 0.01 ug/m2/h, compared to the other panels which all cover much larger ranges. Do you instead mean the regular occurrence of both positive and negative fluxes?**

   Reply: Yes, we meant bi-directional fluxes. The text was modified to make it more clear.

   P16, L32: "The observed large range in formaldehyde fluxes also indicate ..."

   →

   "The observed apparent bi-directional formaldehyde fluxes also indicate ..."

7. **Comment: 17L10, the model "does not capture the observed abrupt increase in this downward flux between 12:00LT and 16:00LT". The abruptness of this observed change is suspicious, is it a regular feature or is it the result of extreme data from one particular anomalous day that is showing up in the mean? (I agree however with the text on lines 10-13 that given the small fluxes and large uncertainty bars this discrepancy is within error)**

   Reply: The elevated downward flux smaller than -0.005 μg m^{-2} s^{-1} (absolute value larger than 0.005 μg m^{-2} s^{-1}) in the afternoon occurred in 10 days during the whole month. Therefore, it is a regular feature. However, the accuracy on PTR-MS measurements of formaldehyde is questionable because the proton affinity of water and formaldehyde is almost the same as we have mentioned in section 2.2.2. Therefore, we can not say if this feature is natural or results from measurement uncertainties. More measurement data are needed to further clarify the diurnal variation of formaldehyde flux.

8. **Comment: Fig 5, is there no chemical production of acetone from monoterpenes / sesquiterpenes? Terpene oxidation are thought to be a notable source of acetone. Is it just that the timescale for this is long compared to canopy exchange?**

   Reply: Inside the canopy, about 86% of the emitted monoterpenes are transported out of the canopy and only 9% of them are oxidized. Moreover, although 70% of the emitted sesquiterpenes are oxidized, the emission rate of sesquiterpenes is only 20% of monoterpenes. Therefore, the oxidation products from these two groups of precursor gases do not provide enough chemical production of acetone inside the canopy compared to emissions.

9. **Comment: Section 5, except for the last paragraph the summary section is just repeating the findings from earlier. This is not that useful. I suggest streamlining this part to just the most important findings and putting more weight on interpretation / synthesis / next steps.**

   Reply: The summary part was rewritten.

   " Based on the O_3 dry deposition model developed in Zhou et al. (2017), a new multi-layer gas dry deposition model extended from Wesely (1989) and Nguyen et al. (2015) was implemented into the 1D chemical transport model SOSAA. This model enabled the calculation of dry deposition processes within a forest canopy for all the gas compounds included in a chemistry scheme.

Using this model we analysed the monthly-averaged in-canopy sources and sinks of 12 featured BVOCs at SMEAR II in July, 2010. Several general behaviours of the selected BVOCs inside a boreal canopy were revealed. Throughout the whole day, $\sim 86\%$ of monoterpenes and $\sim 93\%$ of isoprene+MBO were transported out of the canopy after emitted from the canopy. However, canopy played as a sink for isoprene+MBO at nighttime when they were not emitted. On the contrary, most of the emitted sesquiterpenes were oxidized inside the canopy with only about 29% ventilated out. For the BVOCs with bi-directional fluxes, e.g., acetaldehyde, methanol, acetone and formaldehyde, a large portion or even all of the emitted gases were removed by dry deposition inside the canopy. The soil deposition contributed over 40% of the overall deposition sink. Moreover, the relative contributions of dry deposition sinks compared to emissions were maximum at dawn when highest RH values occurred. Acetol, pinic acid and BCSOZOH were removed by dry deposition inside the canopy with less than 20% compensated by chemical production, resulting in dominant downward fluxes throughout the whole day. ISOP34NO3 and ISOP34OOH showed similar behaviours as acetol at nighttime. However, at daytime, the chemical productions from isoprene oxidation reactions were comparable with deposition sinks, which could even lead to a slightly upward flux at the canopy top at noon for ISOP34NO3.

The vertical distributions of in-canopy sources and sinks for all the gases had several common features. The vertical distribution of dry deposition onto vegetation surfaces always followed the LAD variation, which peaked at about 0.6 h_c in this study. The peaks of emission sources were at 0.8 to 0.9 h_c which was higher than dry deposition because the attenuated PAR and leaf temperature reduced the emission rate inside the canopy. The vertical profile of chemical sinks for sesquiterpenes were nearly the same as their emissions since they were mostly oxidized right after being emitted. The chemical productions for ISOP34NO3 and ISOP34OOH were maximum around the canopy top where the isoprene emission peaked and the radiation was high.

According to the significance of different source and sink terms, the selected BVOCs were classified into five categories: Cemis (monoterpenes, isoprene+MBO), Cemis-chem (sesquiterpenes), Cemis-depo (acetaldehyde, methanol, acetone, formaldehyde), Cdepo (acetol, pinic acid, BCSOZOH), Cchem-depo (ISOP34OOH, ISOP34NO3), where the subscripts represented the significant terms. Generally speaking, the classifications for these BVOCs were expected to be applicable in other canopy types at least in summertime.

This study has provided a method to quantify the proportion of dry deposition sinks for various BVOCs which can be applied in large-scale models in future. On the basis of the analysis of 12 selected BVOCs or groups of BVOCs in this study, a large amount of other compounds with similar properties can be represented by being classified into the five categories mentioned above. For example, OVOCs most likely belong to categories Cdepo and Cchem-depo, which indicates that dry deposition can not be neglected when their sources and sinks are investigated. In addition, the categories Cemis-chem and Cemis-depo imply that the simulation of individual processes is necessary to help further analyse the measured emission data of such gases, and thus obtain a more accurate estimation of BVOCs exchange.

This study has shown that dry deposition of oxidation products of precursor gases as well as other BVOCs could be a potentially important feature of improving our understanding and quantification of BVOCs exchange. However, such assessments are largely limited by available observations that could further corroborate the correctness of the simulated deposition processes as presented in this study. Furthermore, this study stresses the necessity of applying a canopy exchange modeling system for a detailed analysis of BVOCs exchange regimes within and above a boreal forest canopy, instead of applying a big-leaf representation without considering the interactions between emissions, chemistry, turbulent transport and deposition. ”

10. **Comment: 4L28, state why this measurement point was removed**

Reply: P4, L28-29: “Finally, for each compound one data point was filtered out from 164 measurement data points.”

→

“Finally, for each compound one data point was filtered out from 164 measurement data points due to $\zeta > 1$.”

11. **Comment: 7L1-5, and in the descriptions that follow, it would be helpful to give the units for the different parameters as they are defined.**

    Reply: The units in the whole section 3.2.1 were added. The first paragraph was rewritten according to the comments from Referee #1.

    “The local change of the trace gas concentration at each model layer is determined by the gas emission (Q_{emis}), chemical production and loss (Q_{chem}), gas dry deposition (Q_{depo}), and turbulent transport flowing into or out of this layer (Q_{turb}). Here it should be noted that the positive (negative) Q_{turb} is a gas source (sink) term which indicates that the net effect of transportation increases (decreases) the gas concentration within the local layer. All of these processes are included in a mass conservation equation and are computed independently in the model:

$$\begin{aligned}\frac{\partial[X]}{\partial t} &= Q^t_{emis} + Q^t_{chem} + Q^t_{depo} + Q^t_{turb}\\ Q^t_{depo} &= -[X](\mathrm{LAD}\cdot V_{dveg} + A_s V_{dsoil})\\ Q^t_{turb} &= \frac{\partial}{\partial z}\left(K\frac{\partial[X]}{\partial z}\right)\\ V_{dveg} &= V_{dveg}(r_b, r_{stm}, r_{mes}, r_{cut}, r_{ws}, f_{wet})\\ V_{dsoil} &= V_{dsoil}(r_{bs}, r_{soil})\end{aligned}$$

    Here Q^t_{emis} and Q^t_{chem} are directly calculated from the emission module and chemistry module in SOSAA, respectively. The superscript t represents instantaneous quantity. $[X]$ (ng m^{-3}) is the concentration of gas species X. LAD (m^2 m^{-3}) is the all-sided leaf area density. A_s (m^2 m^{-3}) represents the soil area index (Eq. 17 in Zhou et al., 2017). K (m^2 s^{-1}) is the turbulent diffusivity for scalars. V_{dveg} (m s^{-1}) is the vegetation layer-specific conductance which is a function of r_b (quasi-laminar boundary layer resistance; s m^{-1}), r_{stm} (stomatal resistance; s m^{-1}), r_{mes} (mesophyllic resistance; s m^{-1}), r_{cut} (dry cuticular resistance; s m^{-1}), r_{ws} (resistance to leaf wet skin; s m^{-1}) and f_{wet} (fraction of wet skin on leaf surface; dimensionless) (see Eqs. 8, 10 − 13 in Zhou et al. (2017)). V_{dsoil} is the soil conductance which is a function of r_{bs} (soil boundary layer resistance; s m^{-1}) and r_{soil} (soil resistance; s m^{-1}) (see Eq. 9 in Zhou et al. (2017)). ”

    P7, L12: “$\mathrm{S_c}$” → “$\mathrm{S_c}$ (dimensionless)”.

    P7, L13: “molecular diffusivity (D_X)” → “molecular diffusivity (D_X; m^2 s^{-1})”.

    P7, L14: “the molar mass ratio” → “the molar mass (g mol^{-1})”.

    P7, L15: “U” → “U (m s^{-1})”.

    P8, L1: “δ_0” → “δ_0 (m)”.

    P8, L2: “u_{*g}” → “u_{*g} (m s^{-1})”.

    P8, L15: “f_0” → “f_0 (dimensionless)”.

    P8, L16: “T_l” → “T_l (K)”.

12. **Comment: Table 1, it seems that for OMT and OSQ that ’other minor monoterpenes’ and ’other minor sesquiterpenes’ should be placed under ’remarks’ and C10H16, C15H24 should be placed under formula.**

Reply: Table 1: “other minor monoterpenes” and “other minor sesquiterpenes” were moved to the Remark column. “$C_{10}H_{16}$” and “$C_{15}H_{24}$” were added in the Formula column.

13. **Comment: Fig. 2, consider putting a 2nd x-axis on the wind plot for the day and night values to avoid confusion as the night values are shifted by 2m/s**

    Reply: Figure 2a was replotted with a 2nd x-axis for the nighttime wind values (figures are placed at last).

14. **Comment: 15L1-8 and Fig. 2, please expand the temperature plot horizontally so the vertical gradients are more apparent. Right now it is too compressed to really see the changes that are discussed on page 15.**

    Reply: Figure 2b was replotted with larger extension in x direction (figures are placed at last).

15. **Comment: 15L2-3, since you're using temperature as a proxy for potential temperature I suggest parenthetically pointing out the largest difference between the two (I think $\sim$ 0.3K for 36m) and that the observed gradients are larger than this, justifying the approximation**

    Reply: P15, L2-3: “Hence, the air temperature can be assumed to be the potential temperature within this vertical range.”

    →

    “Hence, the air temperature can be assumed to be the potential temperature within this vertical range (the largest difference between potential temperature and T at 36 m is about 0.35 K which is smaller than the observed gradients).”

16. **Comment: 15L8, typo 'buoyancy'**

    Reply: P15, L8: “buoancy” → “buoyancy”.

17. **Comment: Fig 3, the points for daytime measured SH fluxes are hard to see as they fall under the LH points. Consider changing color or symbol to make them more visible.**

    Reply: Figure 3 was replotted to make SH more clear (figures are placed at last).

18. **Comment: Fig. 4, top row missing y-axis title / label**

    Reply: A description was added in captions for Figs. 4, 6 and 8: “The x labels and y labels of the left bottom subfigure also apply to all the other subfigures.”

References

Karl, T., Harley, P., Guenther, A., Rasmussen, R., Baker, B., Jardine, K., and Nemitz, E. (2005). The bi-directional exchange of oxygenated VOCs between a loblolly pine (Pinus taeda) plantation and the atmosphere. *Atmospheric Chemistry and Physics*, 5(11):3015–3031.

Laffineur, Q., Aubinet, M., Schoon, N., Amelynck, C., Müller, J.-F., Dewulf, J., Van Langenhove, H., Steppe, K., and Heinesch, B. (2012). Abiotic and biotic control of methanol exchanges in a temperate mixed forest. *Atmospheric Chemistry and Physics*, 12(1):577–590.

Mogensen, D., Gierens, R., Crowley, J. N., Keronen, P., Smolander, S., Sogachev, A., Nölscher, A. C., Zhou, L., Kulmala, M., Tang, M. J., Williams, J., and Boy, M. (2015). Simulations of atmospheric oh, o_3 and no_3 reactivities within and above the boreal forest. *Atmos. Chem. Phys.*, 15:3909–3932.

Nguyen, T. B., Crounse, J. D., Teng, A. P., St. Clair, J. M., Paulot, F., Wolfe, G. M., and Wennberg, P. O. (2015). Rapid deposition of oxidized biogenic compounds to a temperate forest. *PNAS*, 112(5):E392–E401.

Rantala, P., Aalto, J., Taipale, R., Ruuskanen, T. M., and Rinne, J. (2015). Annual cycle of volatile organic compound exchange between a boreal pine forest and the atmosphere. *Biogeosciences*, 12(19):5753–5770.

Wesely, M. L. (1989). Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models. *Atmos. Env.*, 23:1293–1304.

Zhou, P., Ganzeveld, L., Rannik, Ü., Zhou, L., Gierens, R., Taipale, D., Mammarella, I., and Boy, M. (2017). Simulating ozone dry deposition at a boreal forest with a multi-layer canopy deposition model. *Atmospheric Chemistry and Physics*, 17:1361–1379.

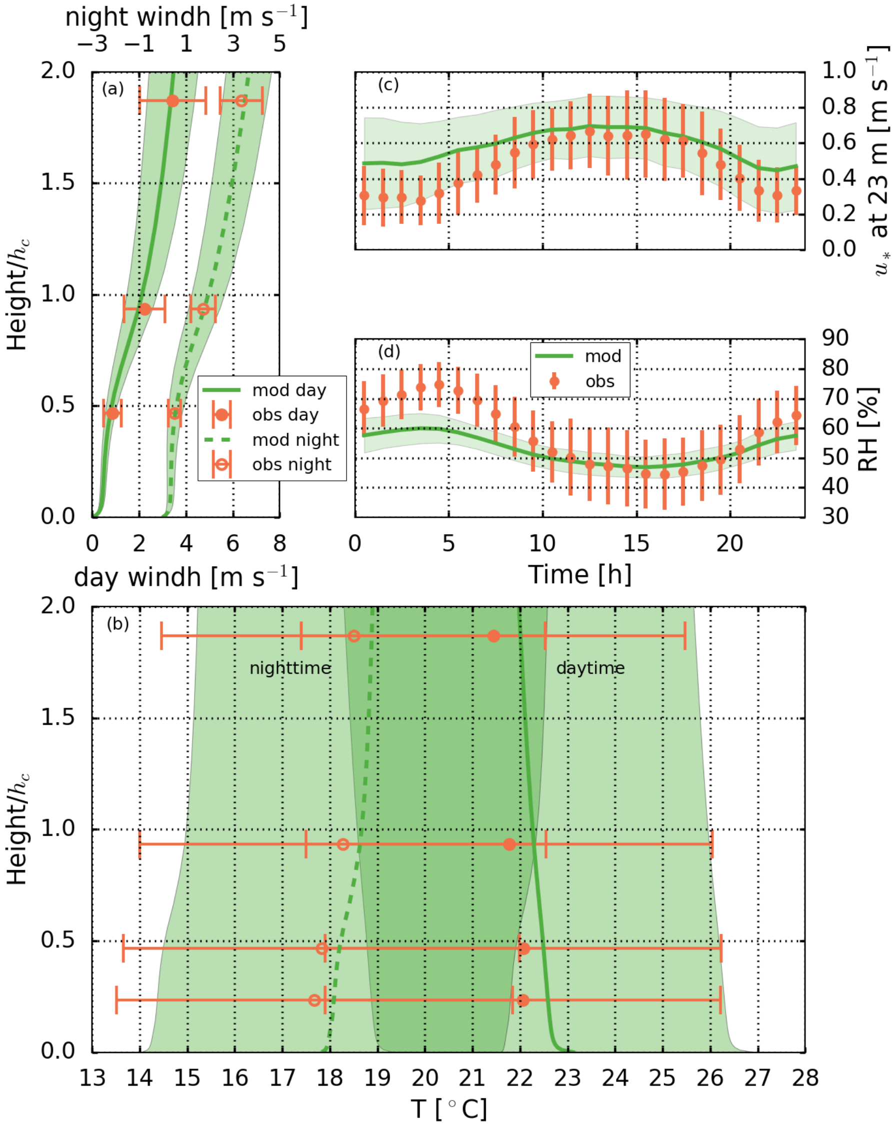

Figure 2: Modeled (green solid line for daytime, green dashed line for nighttime) and measured (yellow solid circle for daytime, yellow empty circle for nighttime) profiles of (a) horizontal wind speed (windh) and (b) air temperature (T). The ranges of ±1 SD (standard deviation) of modeled and measured data are marked as shades and error bars. The height is normalised by canopy height (h_c). The monthly-averaged diurnal cycles of modeled (green line) and measured (yellow dots) (c) friction velocity (u_*) at 23 m and (d) mean RH inside the canopoy are also plotted. The ranges of ±1 SD of modeled and measured data are marked as shades and vertical lines.

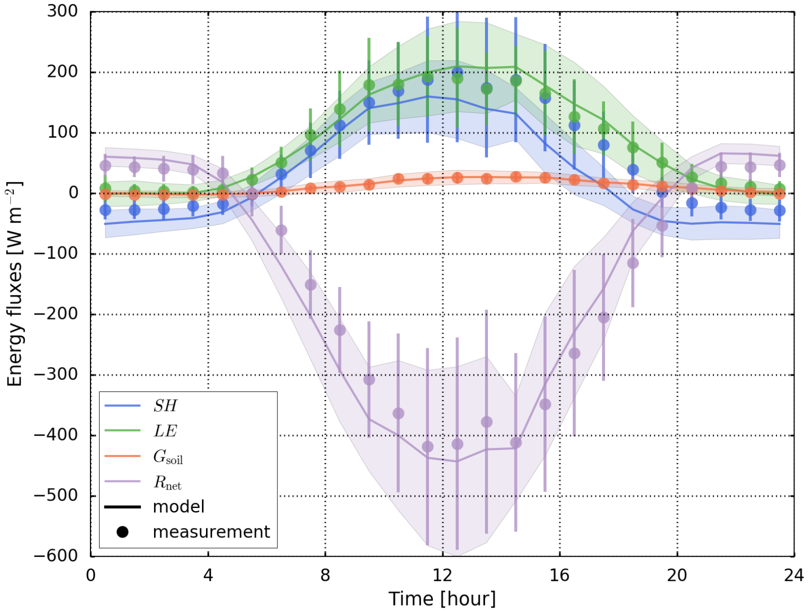

Figure 3: The modeled (solid lines) and measured (points) monthly-averaged diurnal cycles of sensible heat flux (SH, blue), latent heat flux (LE, green), soil heat flux (G_{soil}, yellow) and upward net radiation (R_{net}, purple, the observed R_{net} is at 67 m). The ranges of ±1 standard deviation for modeled and measured data are marked by shaded areas and vertical lines, respectively.