Supplemental Material

In-canopy source/sink model

Bash et al. (2010) describe a first-order closure model that analytically links the NH_3 sources and sinks $S(z)$ within the canopy to the mean concentration profile ($\partial C/\partial z$), momentum absorption by the canopy drag elements, mixing length (L_m), and the friction velocity (u_*) just above the height of the canopy (h_c):

$$S(z)=\begin{cases}-\dfrac{u_*}{\Pr}\exp\left[\beta\left(\dfrac{z-h_c}{L}\right)\right]\left(L_m\dfrac{\partial^2\overline{C}}{\partial z^2}+\beta\dfrac{\partial\overline{C}}{\partial z}\right); & z/h_c\le 1\\ 0; & z/h_c>1\end{cases} \tag{S1}$$

The stability corrected log-linear mean wind speed profile was used to scale the wind speed measured at 2.5 and 3.5 m to the canopy height ($z = h_c$) following Byun (1990)

$$\overline{U}(h_c)=\frac{u_*}{k}\left(\ln\left[\frac{z-d}{z_o}\right]+\psi\left(\frac{z-d}{L}\right)-\psi\left(\frac{z_0}{L}\right)\right)\Bigg|_{z>h_c}, \tag{S2}$$

where z_o is the momentum roughness length, d is the zero plane displacement (estimated as 0.1 h_c and *2/3* h_c respectively), k = 0.4 is von Karman's constant, and ψ is the integrated diabatic stability correction.

The in-canopy mean wind speed ($\overline{U}$) profile, turbulent diffusivity for momentum (K_t), and momentum flux ($\overline{u'w'}$) are based on the analytical solution of Inoue (1963) following the parameterization of Harman and Finnigan (2007):

$$\begin{aligned}\overline{U}(z)&=\overline{U}(h_c)\exp\left[\frac{\beta(z-h_c)}{L_m}\right]\Bigg|_{z<h_c}\\ K_t&=\beta L_m\overline{U}(z)\\ \overline{u'w'}&=-\left(\beta\overline{U}(z)\right)^2\end{aligned}, \tag{S3}$$

The mixing length is parameterized following Harman and Finnigan (2007):

$$L_m = \frac{2\beta^3}{C_d a(z)\varphi_m\left(\frac{h_c - d}{L}\right)}, \tag{S4}$$

where β is the dimensionless momentum flux $\left(u_* / \overline{U}\big|_{z=h_c}\right)$, C_d is the product of the in-canopy drag coefficient and the sheltering factor, a is the mean leaf area density estimated from the ratio of the plant area index to the canopy height (h_c), L is the Obukhov length and φ_m is the dimensionless correction factor for stability.

The model was evaluated by comparing sensible heat fluxes estimated by integrating the source-sink profile of the analytical closure model from the soil surface up to the canopy height to measured above- and in-canopy eddy covariance sensible heat flux measurements (N = 323). Comparison of above-canopy fluxes by regression analysis indicated a linear relationship with a slope of 1.05 and intercept of -8.30 × 10-3 °C m s^{-1} ($r^2 = 0.854$, $p < 0.001$, N = 341); mean normalized bias and error were -21 and 50%, respectively. Comparison of in-canopy measured and modeled fluxes yielded a slope of 0.646 and intercept of -1.72 × 10-3 °C m s^{-1} ($r^2 = 0.632$, $p < 0.001$, N = 341) with mean normalized bias and error of -49 and 59%, respectively. In-canopy sensible heat fluxes were underestimated during the midday peak, which may result from the model assumption of negligible soil heat storage.

We note that a comparison to sensible heat flux may represent a worst-case measure of performance in comparison to NH_3. The vertical gradients of temperature within the canopy are small compared to NH_3. Furthermore, model assumptions of: 1) negligible canopy and soil heat storage and 2) that the direction of the flux can be inferred from the mean air temperature gradient are not satisfied during periods of rapid heating and cooling of the soil/canopy system. Comparison of measured and modeled net canopy-scale NH_3 fluxes showed generally good agreement. Linear regression yielded a slope of 0.882 ($p < 0.001$, N = 15), with modeled fluxes slightly higher than measured fluxes, and an intercept that was not statistically different from zero.

References

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