Atmos. Chem. Phys. Discuss., 15, 779–806, 2015
www.atmos-chem-phys-discuss.net/15/779/2015/
doi:10.5194/acpd-15-779-2015

Atmospheric Chemistry and Physics
Discussions
Open Access

A modified micrometeorological gradient method for estimating O_3 dry deposition over a forest canopy

Z. Y. Wu[1], L. Zhang[1], X. M. Wang[2], and J. W. Munger[3]

[1]Air Quality Research Division, Science and Technology Branch, Environment Canada, Toronto, Canada
[2]School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou, China
[3]School of Engineering and Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA

Received: 26 August 2014 – Accepted: 13 December 2014 – Published: 8 January 2015

Correspondence to: L. Zhang (leiming.zhang@ec.gc.ca)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Small pollutant concentration gradients between levels above a plant canopy result in large uncertainties in estimated air–surface exchange fluxes when using existing micrometeorological gradient methods, including the aerodynamic gradient method (AGM) and the modified Bowen-Ratio method (MBR). A modified micrometeorological gradient method (MGM) is proposed in this study for estimating O_3 dry deposition fluxes over a forest canopy using concentration gradients between a level above and a level below the canopy top, taking advantage of relatively large gradients between these levels due to significant pollutant uptake at top layers of the canopy. The new method is compared with the AGM and MBR methods and is also evaluated using eddy-covariance (EC) flux measurements collected at the Harvard Forest Environmental Measurement Site, Massachusetts during 1993–2000. All the three gradient methods (AGM, MBR and MGM) produced similar diurnal cycles of O_3 dry deposition velocity ($V_d(O_3)$) to the EC measurements, with the MGM method being the closest in magnitude to the EC measurements. The multi-year average $V_d(O_3)$ differed significantly between these methods, with the AGM, MBR and MGM method being 2.28, 1.45 and 1.18 times of that of the EC. Sensitivity experiments identified several input parameters for the MGM method as first-order parameters that affect the estimated $V_d(O_3)$. A 10 % uncertainty in the wind speed attenuation coefficient or canopy displacement height can cause about 10 % uncertainty in the estimated $V_d(O_3)$. An unrealistic leaf area density vertical profile can cause an uncertainty of a factor of 2.0 in the estimated $V_d(O_3)$. Other input parameters or formulas for stability functions only caused an uncertainly of a few percent. The new method provides an alternative approach in monitoring/estimating long-term deposition fluxes of similar pollutants over tall canopies.

1 Introduction

Quantifying atmospheric dry and wet deposition of critical pollutants is important in assessing their life time in air and their potential impact on various ecosystems. In chemical transport models and in monitoring networks, dry deposition is commonly estimated using the so-called inferential method, which requires a parameter – dry deposition velocity (V_d) typically calculated using empirically developed dry deposition algorithms (Wesely and Hicks, 2000; Pleim and Ran, 2011). Existing dry deposition algorithms have large uncertainties, e.g., a factor of 2.0 on long-term basis for several commonly studied species (Flechard et al., 2011; Schwede et al., 2011; Wu et al., 2011, 2012; Matsuda et al., 2006). Field flux measurements are still needed to reduce these uncertainties.

Measurements of O_3 dry deposition flux mostly rely on micrometeorological methods (Wesely and Hicks, 2000). Two types of methods are commonly used: the eddy-covariance technique and the flux-gradient methods. Eddy-covariance (EC) is a direct measurement method determining turbulent fluxes without application of any empirical assumption (Baldocchi et al., 1988; Stella et al., 2012). It has been extensively used to estimate turbulent fluxes of momentum, heat, and trace gases (e.g., CO_2, H_2O, SO_2, O_3) (Baldocchi et al., 2001; Turnipseed et al., 2009; Guenther et al., 2011). However, application of EC is often limited by the difficulty of making high-quality measurements at sufficiently high frequencies (i.e. > 1 Hz) to resolve the covariance between vertical wind velocity and scalar concentration fluctuation (Jacob, 1999). Besides, EC method is costive and complex for maintenance.

A flux-gradient theory approach, also known as K-theory, was used as an alternative method to determine fluxes of gases which lack the fast response instrument for the EC measurement (Meyers et al., 1996; Park et al., 2014). Flux-gradient theory assumes that the turbulence flux is proportional to the production of the mean vertical concentration gradient and an eddy diffusivity (K) (Baldocchi et al., 1988). The derivation of eddy diffusivity for air pollutants currently relies on the similarity assumption which needs more verification from filed measurements. Another critical aspect when employing the flux-gradient theory is to measure the concentrations of gases at different heights with sufficient accuracy and precision (Stella et al., 2012; Loubet et al., 2013). Usually measurements at two adjacent levels above a canopy are used to derive the gradient, e.g., the aerodynamic gradient method (AGM) and the modified Bowen-Ratio approach (MBR). Due to the small concentration gradient above the canopy and the instrument measurement uncertainties, using the flux-gradient method can cause larger uncertainties in estimated dry deposition fluxes.

On the other hand, gradients between levels above and below the canopy top are usually sufficiently large due to the significant sink at top layers of forest canopies. Thus, if concentration gradients at levels above and below the canopy top can be used for estimating dry deposition flux, the uncertainties might be smaller. The present study aims to develop and evaluate such a method (hereafter referred to as the modified gradient method – MGM). It should be noted that this method is still based on the flux-gradient theory.

Long-term concurrent measurements of eddy-covariance fluxes and concentration profiles for O_3 and CO_2 have been conducted at the Harvard Forest Environmental Measurement Site (HFEMS) since 1990 (Munger et al., 1996; Urbanski et al., 2007). This data set enables us to estimate O_3 dry deposition using existing (AGM, MBR and EC) and newly proposed (MGM) methods and thus to evaluate the applicability and uncertainties in all the methods. The micrometeorological methods are briefly described in Sect. 2, the measurement data in Sect. 3, comparison results and sensitivity tests in Sect. 4, and major conclusions and recommendations in Sect. 5.

2 Micrometeorological methods of O_3 flux measurement

2.1 Eddy-covariance technique (EC)

EC determines the turbulent flux (F) by calculating the covariance between vertical wind velocity (w) and concentration of the gas (c):

$$F = \overline{w'c'} \tag{1}$$

where the over-bar denotes the time average and the primes denote fluctuations from the mean ($x' = x(t) - \overline{x}$, $\overline{x}$ = mean). By convention, a positive flux is upward (emission) and negative flux is downward (deposition).

2.2 Aerodynamic gradient method (AGM)

With an assumption that turbulent transport is analogous to molecular diffusion (Baldocchi et al., 1988), the flux-gradient theory is theoretically described as follows:

$$F = -K_c(z)\mathrm{d}C/\mathrm{d}z \tag{2}$$

where K_c is the eddy diffusivity for the gas, and $\mathrm{d}C/\mathrm{d}z$ is the vertical concentration gradient of the gas. Two of the more popular methods for calculating K_c are the aerodynamic gradient method (AGM) and the modified Bowen-Ratio approach (MBR).

The AGM method assumes that heat and mass are transported in a similar way within a well-developed surface layer (Erisman and Draaijers, 1995). K_c is related to the interstitial aerodynamic resistance (R_a) (Baldocchi, 1988) as

$$R_\mathrm{a}(z_1 : z_2) = \int_{z_2}^{z_1} \mathrm{d}z/K_c(z) \tag{3}$$

where z_1 and z_2 indicate the heights of adjacent levels above canopy ($z_1 > z_2$).

Using Eqs. (2) and (3), the deposition flux (F) is determined as:

$$F = -\frac{\Delta C}{R_a(z_1:z_2)} = -\frac{C_1 - C_2}{R_a(z_1:z_2)} \tag{4}$$

C_1 and C_2 indicate the gas concentrations at z_1 and z_2, respectively. R_a is calculated as

$$R_a(z_1:z_2) = (\kappa u_*)^{-1}\left[\ln\frac{z_1-d}{z_2-d} + \psi_h\left(\frac{z_1-d}{L}\right) - \psi_h\left(\frac{z_2-d}{L}\right)\right] \tag{5}$$

where κ is the von Karman's constant (0.4), u_* the friction velocity, d the zero-plane displacement height, L the Obukhov length, and ψ_h the integrated stability correction function for heat using those proposed by Businger et al. (1971) and modified by Högström (1988).

2.3 Modified Bowen-Ratio Method (MBR)

The MBR method is also based on the flux-gradient theory (Eq. 2), but the eddy diffusivity (K_c) is derived from flux and gradient measurements of another scalar (e.g., sensible heat, CO_2, H_2O) and assumes it is equal to K_c of the gas of interest. In this study, the flux and gradient measurements of CO_2 are available at the same heights of O_3, so K_c of O_3 was calculated from the CO_2 measurements as follows:

$$K_c = K_{CO_2} = -F_{CO_2}\Delta z/\Delta C(CO_2) \tag{6}$$

where K_{CO_2} is the eddy diffusivity of CO_2, F_{CO_2} is the eddy-covariance flux of CO_2, $\Delta C(CO_2)$ is the concentration gradient of CO_2 over the same height interval as $\Delta C(O_3)$, and Δz is the height interval of concentration measurements.

Using Eqs. (2) and (6), the O_3 flux (F) is calculated as:

$$F = F_{CO_2}\Delta C(O_3)/\Delta C(CO_2) \tag{7}$$

2.4 Modified gradient method (MGM)

The newly proposed MGM method is also based on the flux-gradient theory (Eq. 2). While the flux-gradient theory has been long questioned within plant canopy environment due to the infrequent but predominant large eddies within canopy (Wilson, 1989; Raupach, 1989), it may be valid for estimating O_3 exchange in the upper portion of a tall canopy because the concentration gradient is large in the upper portion of a tall canopy where most of the O_3 uptake occurs and the vertical length scale of turbulence are probably smaller than the distance associated with changes in the concentration and wind speed gradients (Baldocchi, 1988). The flux-gradient theory approach has been used to estimate the vertical flux profile of air pollutants within plant canopy (e.g., Baldocchi, 1988; Bash et al., 2010). Similar to the flux-gradient theory applied in the constant flux layer above canopy, a height-dependent flux ($F(z)$) within canopy is computed as:

$$F(z) = -K_c(z)\frac{\mathrm{d}C}{\mathrm{d}z} \tag{8}$$

where $z \le h$. Based on Eq. (8), the O_3 flux at canopy top ($F(h)$) is defined as

$$F(h) = -\frac{C_h - C_3}{R_\mathrm{a}(h:z_3)} \tag{9}$$

where C_h and C_3 are the concentrations at canopy top (h) and the height of z_3 ($z_3 < h$), respectively. $R_\mathrm{a}(h:z_3)$ is related to K_c as

$$R_\mathrm{a}(h:z_3) = \int_{z_3}^{h} \mathrm{d}z/K_c(z) \tag{10}$$

According to the aerodynamic gradient method (Eq. 4), the O_3 flux above canopy can be calculated from the concentration gradient between the reference height z_1 and the canopy top h ($z_1 > h$) as follows:

$$F = -\frac{C_1 - C_h}{R_\mathrm{a}(z_1 : h)} \tag{11}$$

And based on the assumption of a constant flux layer in the near surface layer, the O_3 flux above canopy calculated in Eq. (11) should be equal to the O_3 flux at canopy top derived from Eq. (9). Using Eqs. (9) and (11), we can derive that:

$$F = -\frac{C_1 - C_3}{R_\mathrm{a}(z_1 : h) + R_\mathrm{a}(h : z_3)} \tag{12}$$

$R_\mathrm{a}(z_1 : h)$ is calculated by Eq. (5). $R_\mathrm{a}(h : z_3)$ is computed as the vertical integration of within canopy eddy diffusivity ($K_c(z)$), as shown in Eq. (10).

$K_c(z)$ is assumed to equal $0.8K_m(z)$, which is the within canopy eddy diffusivity for momentum transfer (Halldin and Lindroth, 1986). As described in Baldocchi (1988), $K_m(z)$ is determined as

$$K_m(z) = \frac{\int_0^z C_m(z)a(z)u(z)^2 \mathrm{d}z}{\mathrm{d}u(z)/\mathrm{d}z} \tag{13}$$

where $a(z)$ is the leaf area density at height z, and $u(z)$ is the horizontal wind speed within canopy. Similar to Baldocchi (1988), $K_m(z)$ is assumed to be constant below crown closure (about $0.7h$) and equal to K_m at $0.7h$. Thus we suggest here that the level of concentration measurement below canopy (z_3) should not be lower that the crown closure of canopy.

The effective drag coefficient ($C_m(z)$) is assumed to be constant with height (see Thom, 1975) following Baldocchi (1988):

$$C_m(z) = \frac{C_\mathrm{am}}{\mathrm{LAI}\left[u_m/u(z_1)\right]^2} \tag{14}$$

where LAI is the canopy leaf area index, u_m the mean wind speed within canopy, and $u(z_1)$ the wind speed at the reference height z_1. The bulk canopy drag coefficient (C_{am}) is computed as

$$C_{\mathrm{am}} = u_*^2/u(z_1)^2 \tag{15}$$

The mean within canopy wind speed (u_m) is calculated as

$$u_m = (1/h)\int_0^h u(z)\mathrm{d}z \tag{16}$$

Within canopy wind speed profile ($u(z)$) follows Cionco (1972):

$$u(z) = u_h e^{-\alpha(1-z/h)} \tag{17}$$

where u_h is wind speed at the canopy top, and α is wind speed attenuation coefficient. The above canopy logarithmic wind profile is used to scale the wind speed measured at the reference height z_1 to the canopy height h:

$$u_h = u(z_1)\frac{\ln(h-d) - \ln(z_0) + \psi_{\mathrm{m}}[(h-d)/L] - \psi_{\mathrm{m}}[z_0/L]}{\ln(z_1-d) - \ln(z_0) + \psi_{\mathrm{m}}[(z_1-d)/L] - \psi_{\mathrm{m}}[z_0/L]} \tag{18}$$

where z_0 is the roughness length for momentum, and ψ_{m} is the integrated stability correction function for momentum as proposed by Businger et al. (1971) and modified by Högström (1988).

Assuming a zero concentration on the absorbing surface, the dry deposition velocity (V_{d}) of O_3 can be determined as

$$V_{\mathrm{d}} = -F/C(z_1) \tag{19}$$

where $C(z_1)$ is the O_3 concentration measured at the reference height z_1.

3 Field measurements used in this study

3.1 Site description

The Harvard Forest Environmental Measurement Site (HFEMS) (42.54° N, 72.18° W) is located in central Massachusetts at an elevation of 340 m above sea level. The forest is 80-year-old on average, which consists of red maple (*Acer rubrum*) and red oak (*Quercus rubra*) with scattered stands of Eastern hemlock (*Tsuga canadensis*), red pine (*Pinus resinosa*) and white pine (*Pinus strobus*). The canopy height near the observation tower is up to 23 m with a peak leaf area index (*LAI*) of $\sim 5.0\,\mathrm{m^2\,m^{-2}}$ during summer. The nearest sources of significant pollution are a secondary road about 2 km to the west of the site and a main highway about 5 km to the north.

A permanent 30 m Rohn 25G tower has been utilized at HFEMS to measure eddy-covariance fluxes of sensible heat, H_2O, momentum, CO_2, and O_3, along with vertical profiles of CO_2 and O_3 since 1990 (Fig. 1). Eddy-covariance fluxes were measured at a height of 29 m above the ground. For the profile measurements air was continuously sampled from heights of 29, 24.1, 18.3, 12.7, 7.5, 4.5, 0.8, and 0.3 m a.g.l. to determine the concentrations of CO_2 and O_3. In this study, the upper three levels were used to derive the gradients. Details on the site and the instrumental methods can be found in Munger et al. (1996). Data used in this study are available online at http://atmos.seas.harvard.edu/lab/data/nigec-data.html.

Zhao et al. (2011) retrieved the vertical profile of leaf area density at Harvard Forest from a ground-based lidar scanning. Two tree species groups (i.e. Hardwood and Conifer) were chosen. According to the species composition around the measurement tower, the average leaf area density used in this study was calculated as 75 % of that of Hardwood and 25 % of that of Conifer from Zhao et al. (2011), as shown in Fig. 1.

The monthly averaged leaf area index (LAI) at HFEMS was derived from the ground-based measurements for most years between 1998 and 2013 using the LICOR LAI-2000 system at 30–40 plots around the tower (Urbanski et al., 2007). The measurements during January and February were not available whose values were obtained based on extrapolation (Fig. 2). The roughness length (z_0) and displacement height (d) were calculated as a function of canopy height (h) and LAI, following Meyers et al. (1998) (see Fig. 2):

$$z_0 = h(0.215 - \mathrm{LAI}^{0.25}/10) \tag{20}$$

$$d = h(0.1 + \mathrm{LAI}^{0.2}/2) \tag{21}$$

3.2 Data selection

A total of 10 252 hourly measuring points, recorded at HFEMS during 1993–2000, were screened to eliminate the influence of periods associated with instrumental and measurement problems and violation of the use of the flux-gradient theory.

In order to reduce the random measurement error in the concentration gradient, O_3 concentrations below 1 ppbv were rejected, resulting in approximately 0.1 % of the data being omitted. In addition, periods with $[O_3] < [NO_y]$ (1.9 %) were excluded to avoid periods when O_3 chemical reactions may exceed O_3 deposition (Munger et al., 1996). Wind speed below $1.0\,\mathrm{m\,s^{-1}}$ (1.2 %) and drag coefficient below 0.02 (6.6 %) were removed because of probable invalid flux–gradient relationships (Feliciano et al., 2001). Outliers in the data (2.9 %) were removed, omitting any deposition velocity exceeding the maximum achievable deposition velocity $V_{d,\max}$ ($V_{d,\max} = 1/(R_a + R_b)$), by more than a factor of 1.5 (Matsuda et al., 2006). Periods with counter-gradient profiles (69.8 %) which represent a downward flux (from EC measurement) while with a negative gradient (upper level minus lower level) or vice versa were rejected (Park et al., 2014). A total of 74.0 % of the data was omitted in the following analysis. This percentage value is slightly smaller than the sum of those from all the criteria due to the overlap of some data points between the criteria.

Figure 3 shows the mean diurnal cycles of O_3 concentration at different heights derived from the original dataset and from the data after selection. The O_3 concentration increased during the early morning to reach a daily maximum of over 40 ppbv in the early afternoon and then decreased to ∼ 30 ppbv at night. As shown in Fig. 3a, the gradient between the two heights above canopy (i.e. 29 and 24.1 m) was only about 0.4 ppbv on average, smaller than that between the levels above canopy (24.1 m) and inside canopy (18.3 m) (∼ 0.8 ppbv). The gradients were relatively small during the morning (e.g., 0.1 ppbv at 11:00 LST) compared to the other periods of the day. Photochemical reactions could be intensive in the morning due to accumulation of O_3 precursors in the surface layer during the night, which may exhibit a significant influence on the vertical profiles of O_3 (Keronen et al., 2003). After screening the data with the criteria, the gradients among these three levels were significantly larger, reaching up to 1.0 and 1.6 ppbv, respectively (see Fig. 3b).

4 Results and discussion

4.1 Comparison of $V_d(O_3)$ by the eddy-covariance and gradient methods

O_3 dry deposition velocity ($V_d(O_3)$) measured by the eddy-covariance (EC) technique at Harvard Forest typically ranged from 0.14–0.53 $cm\,s^{-1}$, with a median value of 0.30 $cm\,s^{-1}$ during the study period (Table 1). Since the screened deposition velocities still include certain outlying data, the mean value was calculated using data between 10th and 90th percentiles in order to reduce the influence of the outlying data. Following this approach, the mean $V_d(O_3)$ by the EC technique was 0.34 $cm\,s^{-1}$, which was significantly smaller than those by the gradient methods (Table 1). The ratios of mean $V_d(O_3)$ by the modified gradient (MGM), modified Bowen-Ratio (MBR), and aerodynamic gradient (AGM) methods to that by the EC technique were 1.18, 1.45 and 2.28, respectively. Previous studies on the inter-comparisons of these methods for O_3 are few and the results varied. Muller et al. (2009) found that the mean $V_d(O_3)$ by the AGM method was 1.60–3.47 times those by the EC technique at a grassland in Southern Scotland. Loubet et al. (2013) showed that the AGM method gave 40 % larger $V_d(O_3)$ than the EC technique over a mature maize field in Paris. Keronen et al. (2003) found that $V_d(O_3)$ by the AGM and EC methods generally agreed well at a Nordic pine forest,

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

and so did Stella et al. (2012) over a bare soil in Paris. Droppo (1985) found close $V_d(O_3)$ values with the MBR and EC methods at a Northeastern US grassland site.

Figure 4 shows the diurnal cycles of $V_d(O_3)$ by the EC and gradient methods. Although the trends were similar, the MBR and AGM $V_d(O_3)$ were consistently larger than the EC $V_d(O_3)$. The EC $V_d(O_3)$ was about 0.2 $\mathrm{cm\,s^{-1}}$ on average during night and reached a daily maximum of 0.5 $\mathrm{cm\,s^{-1}}$ around noon. The $V_d(O_3)$ by the MBR and AGM methods reached around 0.8 and 1.3 $\mathrm{cm\,s^{-1}}$ during the daytime, respectively and remained about 0.4 $\mathrm{cm\,s^{-1}}$ during night. The MGM $V_d(O_3)$ agreed well with the EC $V_d(O_3)$ during the daytime but was slightly larger at night. This discrepancy has been identified in previous studies (Keronen et al., 2003; Stella et al., 2012) and could be due to the fact that nocturnal conditions affect both EC and gradient measurements. The EC technique is found to underestimate flux during calm night-time periods at Harvard Forest (Goulden et al., 1996). The stability correction functions used in the gradient methods are subject to large uncertainties under stable conditions (Högström, 1988).

As shown in Fig. 5, the EC $V_d(O_3)$ exhibited a significant seasonal pattern with peak values in summer ($\sim 0.5\,\mathrm{cm\,s^{-1}}$) and small values in winter (0.15–0.28 $\mathrm{cm\,s^{-1}}$). Both the MGM and MBR methods captured this seasonal cycle, but the MGM method produced a higher $V_d(O_3)$ than the EC technique during winter (December–February) and the MBR method gave a significant overestimation in summer (June–September). The monthly AGM $V_d(O_3)$ was consistently larger than the EC $V_d(O_3)$ and exhibited a less clear seasonal pattern with alternating increases and decreases in the $V_d(O_3)$.

4.2 Sensitivity of $V_d(O_3)$ by the modified gradient method to the key parameters/formulas

As shown in Sect. 4.1, the MGM method performed better than the MBR and AGM methods. This improvement should mainly be attributed to reductions in errors of O_3 concentration gradients. However, the MGM method increased the complexity in the algorithm and added more model parameters, which may in turn increase the uncertainty in the estimated $V_d(O_3)$.

To test the sensitivity of the estimated $V_d(O_3)$ by the MGM method to the key parameters/formulas, experiments were conducted by changing the parameters/formulas within a reasonable range. For some single-value parameters (i.e. roughness length, displacement height, wind speed attenuation coefficient, and leaf area index), sensitivity tests were conducted by increasing or decreasing the value by 10 %.

As shown in Fig. 6 and Table 2, the MGM $V_d(O_3)$ was highly sensitive to the changes in wind speed attenuation coefficient and displacement height. Higher wind speed attenuation coefficient could result in lower within-canopy wind speed (Eq. 17) and thus lower eddy exchange coefficient and $V_d(O_3)$ (Table 2). Based on a least-square fitting of within-canopy wind profiles measured at Harvard Forest for noon-periods in summer, the attenuation coefficient was estimated to be ~ 10.6 at Harvard Forest. Cionco (1972) suggested that the attenuation coefficient varies with leaf area. Therefore, the application of this value throughout the whole year could produce a certain uncertainty in the estimated $V_d(O_3)$.

The MGM $V_d(O_3)$ increased when the displacement height increased or vice versa (Fig. 6, Table 2). Sakai et al. (2001) calculated the displacement height at Harvard Forest using noon-period measurements and indicated the ratio of displacement height to canopy height was 0.77 in summer with foliated canopy and 0.6 in winter with leafless canopy. In this study, we estimated a close value in summer (0.79) and a slightly higher value in winter (0.66) using the method proposed by Meyers et al. (1998) (Fig. 2). The overestimation of the displacement height could partly explain the overestimation of $V_d(O_3)$ by the MGM method during December to February (Fig. 5).

Figure 6 shows that the MGM $V_d(O_3)$ was less sensitive to the changes of roughness length and leaf area index. The relative differences in the estimated $V_d(O_3)$ were less than 2 % when roughness length and leaf area index varied by 10 % (Table 2).

Meyers et al. (1998) provided three typical types of leaf area density profiles, which are significantly different in shape from the profile in Harvard Forest used in this study (see Fig. 7). We conducted sensitivity experiments by replacing the Harvard Forest profile with those in Meyers et al. (1998) to assess the impact of vertical profile of leaf area density on the determination of $V_d(O_3)$. As shown in Fig. 6 and Table 2, the vertical profile of leaf area density impacted the estimated $V_d(O_3)$ greatly, with a relative difference in $V_d(O_3)$ of above 50 %. The profile with higher leaf density in the upper canopy (profile 3) resulted in a higher $V_d(O_3)$ while the profile with abundant understory plants (profile 1) leaded to a lower $V_d(O_3)$.

In this study, the stability correction functions proposed by Businger et al. (1971) and modified by Högström (1988) were used, but several others exist, such as those by Dyer (1974), Paulson (1970), and Webb (1970). Figure 6 indicated that uncertainties in the stability correction functions for heat (ψ_h) and momentum (ψ_m) had little impact on the MGM $V_d(O_3)$ values. The relative difference of V_d was less than 4 % for different ψ_h and less than 1 % for different ψ_m. Stella et al. (2012) found that the variation of $V_d(O_3)$ on different ψ_h was roughly 10 % on average when using the AGM method. ψ_h influences the estimation of V_d due to the impact on the calculation of turbulent transfer above the canopy. As the MGM method considered both the above- and within- canopy turbulence transfer, the MGM $V_d(O_3)$ values were thus less sensitive to the choice of ψ_h.

5 Conclusions and recommendations

A modified micrometeorological gradient method was developed to quantify O_3 dry deposition over a forest canopy making use of concentration gradients between levels above and below the canopy top. The MGM method produced close $V_d(O_3)$ to the eddy-covariance measurements at Harvard Forest during daytime, although slightly overestimated the measurements at night. The modified method seemed to be an improvement compared to the two existing flux-gradient methods (AGM and MBR) in terms of predicted long-term mean, diurnal and seasonal cycles of $V_d(O_3)$. Sensitivity tests show that model parameters for MGM including wind speed attenuation coefficient, canopy displacement height and vertical distribution of leaf density were first-order parameters affecting the estimated $V_d(O_3)$. Model results were less sensitive to roughness length, leaf area index, and stability function for heat and momentum.

The newly-developed MGM method has potential to be applied routinely to monitor/estimate long-term deposition fluxes of O_3 and other similar pollutants over tall canopies. The within-canopy measurement should be close to but not lower than the canopy closure height where most of the flux exchange occurs. Key model parameters mentioned above need to be characterized as accurate as possible. For example, seasonal profiles of vertical distribution of leaf area density, canopy displacement height, and vertical wind profile related parameters are needed.

Acknowledgements. This work is funded by the Clean Air and Regulatory Agenda program. X. M. Wang is supported by the Natural Science Foundation of China (grant 41275018).

References

Baldocchi, D.: A multi-layer model for estimating sulfur dioxide deposition to a deciduous oak forest canopy, Atmos. Environ., 22, 869–884, 1988.

Baldocchi, D. D., Hincks, B. B., and Meyers, T. P.: Measuring biosphere–atmosphere exchanges of biologically related gases with micrometeorological methods, Ecology, 69, 1331–1340, 1988.

Baldocchi, D., Falge, E., Gu, L., Olson, R., Hollinger, D., Running, S., Anthoni, P., Bernhofer, C., Davis, K., and Evans, R.: FLUXNET: a new tool to study the temporal and spatial variability of ecosystem-scale carbon dioxide, water vapor, and energy flux densities, B. Am. Meteorol. Soc., 82, 2415–2434, 2001.

Bash, J. O., Walker, J. T., Katul, G. G., Jones, M. R., Nemitz, E., and Robarge, W. P.: Estimation of in-canopy ammonia sources and sinks in a fertilized Zea Mays field, Environ. Sci. Technol., 44, 1683–1689, 2010.

Businger, J. A., Wyngaard, J. C., Izumi, Y., and Bradley, E. F.: Flux–profile relationships in the atmospheric surface layer, J. Atmos. Sci., 28, 181–189, 1971.

Cionco, R. M.: A wind-profile index for canopy flow, Bound.-Lay. Meteorol., 3, 255–263, 1972.

Droppo, J. G.: Concurrent measurements of ozone dry deposition using eddy correlation and profile flux methods, J. Geophys. Res., 90, 2111–2118, 1985.

Erisman, J. W. and Draaijers, G. P. J.: Atmospheric Deposition in Relation to Acidification and Eutrophication, in: Studies in Environmental Science, 63, Elsevier, Amsterdam, 64–66, 1995.

Feliciano, M., Pio, C., and Vermeulen, A.: Evaluation of SO_2 dry deposition over short vegetation in Portugal, Atmos. Environ., 35, 3633–3643, 2001.

Flechard, C. R., Nemitz, E., Smith, R. I., Fowler, D., Vermeulen, A. T., Bleeker, A., Erisman, J. W., Simpson, D., Zhang, L., Tang, Y. S., and Sutton, M. A.: Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network, Atmos. Chem. Phys., 11, 2703–2728, doi:10.5194/acp-11-2703-2011, 2011.

Goulden, M. L., Munger, J. W., Fan, S. M., Daube, B. C., and Wofsy, S. C.: Measurements of carbon sequestration by long-term eddy covariance: methods and a critical evaluation of accuracy, Glob. Change Biol., 2, 169–182, 1996.

Guenther, A., Kulmala, M., Turnipseed, A., Rinne, J., Sun, T., and Reissell, A.: Integrated land ecosystem-atmosphere processes study (iLEAPS) assessment of global observational networks, Boreal Environ. Res., 16, 321–336, 2011.

Halldin, S. and Lindroth, A.: Pine forest microclimate simulation using different diffusivities, Bound.-Lay. Meteorol., 35, 103–123, 1986.

Högström, U.: Non-dimensional wind and temperature profiles in the atmospheric surface layer: a re-evaluation, Bound.-Lay. Meteorol., 42, 55–78, 1988.

Jacob, D.: Introduction to Atmospheric Chemistry, Princeton University Press, New Jersey, 64 pp., 1999.

Keronen, P., Reissell, A., Rannik, U., Pohja, T., Siivola, E., Hiltunen, V., Hari, P., Kulmala, M., and Vesala, T.: Ozone flux measurements over a Scots pine forest using eddy covariance method: performance evaluation and comparison with flux-profile method, Boreal Environ. Res., 8, 425–444, 2003.

Loubet, B., Cellier, P., Fléchard, C., Zurfluh, O., Irvine, M., Lamaud, E., Stella, P., Roche, R., Durand, B., and Flura, D.: Investigating discrepancies in heat, CO_2 fluxes and O_3 deposition velocity over maize as measured by the eddy-covariance and the aerodynamic gradient methods, Agr. Forest Meteorol., 169, 35–50, 2013.

Matsuda, K., Watanabe, I., Wingpud, V., Theramongkol, P., and Ohizumi, T.: Deposition velocity of O_3 and SO_2 in the dry and wet season above a tropical forest in northern Thailand, Atmos. Environ., 40, 7557–7564, 2006.

Meyers, T. P., Hall, M. E., Lindberg, S. E., and Kim, K.: Use of the modified Bowen-ratio technique to measure fluxes of trace gases, Atmos. Environ., 30, 3321–3329, 1996.

Meyers, T. P., Finkelstein, P., Clarke, J., Ellestad, T. G., and Sims, P. F.: A multilayer model for inferring dry deposition using standard meteorological measurements, J. Geophys. Res., 103, 22645–22661, 1998.

Muller, J., Coyle, M., Fowler, D., Gallagher, M. W., Nemitz, E. G., and Percival, C. J.: Comparison of ozone fluxes over grassland by gradient and eddy covariance technique, Atmos. Sci. Lett., 10, 164–169, 2009.

Munger, J. W., Wofsy, S. C., Bakwin, P. S., Fan, S. M., Goulden, M. L., Daube, B. C., Goldstein, A. H., Moore, K. E., and Fitzjarrald, D. R.: Atmospheric deposition of reactive nitrogen oxides and ozone in a temperate deciduous forest and a subarctic woodland: 1. Measurements and mechanisms, J. Geophys. Res., 101, 12639–12657, 1996.

Park, J.-H., Fares, S., Weber, R., and Goldstein, A. H.: Biogenic volatile organic compound emissions during BEARPEX 2009 measured by eddy covariance and flux–gradient similarity methods, Atmos. Chem. Phys., 14, 231–244, doi:10.5194/acp-14-231-2014, 2014.

Pleim, J. and Ran, L.: Surface flux modeling for air quality applications, Atmosphere, 2, 271–302, 2011.

Raupach, M.: A practical Lagrangian method for relating scalar concentrations to source distributions in vegetation canopies, Q. J. Roy. Meteor. Soc., 115, 609–632, 1989.

Sakai, R. K., Fitzjarrald, D. R., and Moore, K. E.: Importance of low-frequency contributions to eddy fluxes observed over rough surfaces, J. Appl. Meteorol., 40, 2178–2192, 2001.

Schwede, D., Zhang, L., Vet, R., and Lear, G.: An intercomparison of the deposition models used in the CASTNET and CAPMoN networks, Atmos. Environ., 45, 1337–1346, 2011.

Stella, P., Loubet, B., Laville, P., Lamaud, E., Cazaunau, M., Laufs, S., Bernard, F., Grosselin, B., Mascher, N., Kurtenbach, R., Mellouki, A., Kleffmann, J., and Cellier, P.: Comparison of methods for the determination of NO-O_3-NO_2 fluxes and chemical interactions over a bare soil, Atmos. Meas. Tech., 5, 1241–1257, doi:10.5194/amt-5-1241-2012, 2012.

Thom, A. S.: Momentum, mass and heat exchange of plant communities, in: Vegetation and the Atmosphere, edited by: Monteith, J. L., Academic Press, London, 57–109, 1975.

Turnipseed, A. A., Burns, S. P., Moore, D. J., Hu, J., Guenther, A. B., and Monson, R. K.: Controls over ozone deposition to a high elevation subalpine forest, Agr. Forest Meteorol., 149, 1447–1459, 2009.

Urbanski, S., Barford, C., Wofsy, S., Kucharik, C., Pyle, E., Budney, J., McKain, K., Fitzjarrald, D., Czikowsky, M., and Munger, J.: Factors controlling CO_2 exchange on timescales from hourly to decadal at Harvard Forest, J. Geophys. Res., 112, G02020, doi:10.1029/2006JG000293, 2007.

Wesely, M. and Hicks, B.: A review of the current status of knowledge on dry deposition, Atmos. Environ., 34, 2261–2282, 2000.

Wilson, J. D.: Turbulent transport within the plant canopy, in: Estimation of Areal Evapotranspiration, edited by: Black, T. A., Spittlehouse, D. L., Novak, M. D., and Price, D. T., IAHS Press, Wallingford, UK, 43–80, 1989.

Wu, Z. Y., Wang, X. M., Chen, F., Turnipseed, A. A., Guenther, A. B., Niyogi, D., Charusombat, U., Xia, B. C., Munger, J. W., and Alapaty, K.: Evaluating the calculated dry deposition velocities of reactive nitrogen oxides and ozone from two community models over a temperate deciduous forest, Atmos. Environ., 45, 2663–2674, 2011.

Wu, Z. Y., Wang, X. M., Turnipseed, A. A., Chen, F., Zhang, L. M., Guenther, A. B., Karl, T., Huey, L. G., Niyogi, D., Xia, B. C., and Alapaty, K.: Evaluation and improvements of two community models in simulating dry deposition velocities for peroxyacetyl nitrate (PAN) over a coniferous forest, J. Geophys. Res., D04310, doi:10.1029/2011JD016751, 117, 2012.

Zhao, F., Yang, X., Schull, M. A., Román-Colón, M. O., Yao, T., Wang, Z., Zhang, Q., Jupp, D. L., Lovell, J. L., and Culvenor, D. S.: Measuring effective leaf area index, foliage profile, and stand height in New England forest stands using a full-waveform ground-based lidar, Remote Sens. Environ., 115, 2954–2964, 2011.

Table 1. Statistics on hourly $V_d(O_3)$ (cm s^{-1}) at Harvard Forest during 1993–2000 as measured by the eddy-covariance (EC) and three gradient methods (MGM: the modified gradient method; MBR: the modified Bowen-Ratio method; AGM: the aerodynamic gradient method).

	EC	MGM	MBR	AGM
10th Percentile	0.05	0.09	0.03	0.11
25th Percentile	0.14	0.19	0.12	0.26
Median	0.30	0.35	0.35	0.62
75th Percentile	0.53	0.61	0.85	1.27
90th Percentile	0.83	0.96	1.86	2.28
Mean*	0.34	0.40	0.49	0.77

* The arithmetical mean of data between 10th and 90th percentiles.

Table 2. Relative difference between $V_d(O_3)$ determined by the modified gradient method with different parameters/formulas (%)[a].

	z_0		d		α		LAI		LAD[b]			ψ_h^c			ψ_m^c		
	−10 %	+10 %	−10 %	+10 %	−10 %	+10 %	−10 %	+10 %	Prf 1	Prf 2	Prf 3	D74	P70	W70	D74	P70	W70
Median	−1.1	1.1	−4.8	10.8	10.1	−9.3	−0.6	0.5	−34.4	8.4	57.4	3.1	1.7	0.5	0.2	0.08	0.06
Mean[d]	−1.0	1.1	−4.7	10.4	10.2	−9.6	−0.6	0.5	−34.5	8.4	58.5	3.1	1.4	−0.01	0.1	0.02	−0.01

[a] Relative difference = (Sensitivity − Base)/Base × 100 %.

[b] Vertical profile of leaf area density from Meyers et al. (1998) as shown in Fig. 7.

[c] D74: Dyer (1974); P70: Paulson (1970); W70: Webb (1970).

[d] The arithmetical mean of data between 10th and 90th percentiles.

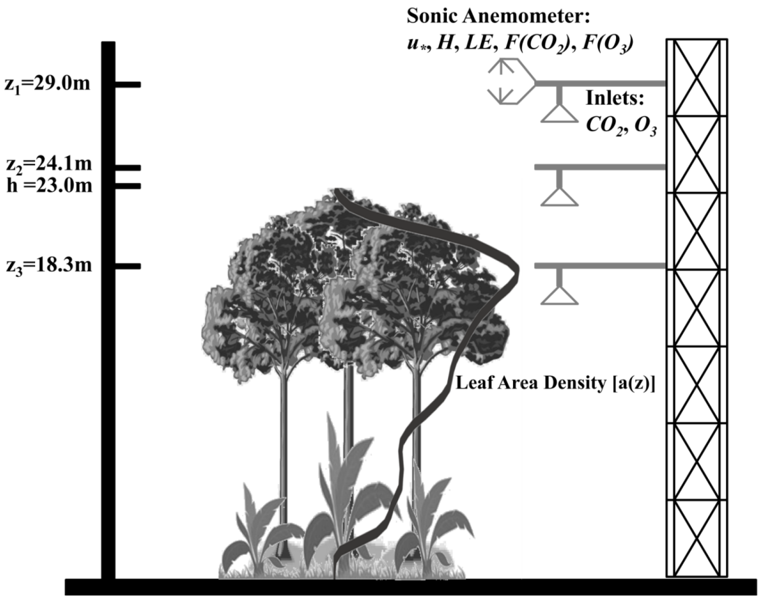

Figure 1. Schematic of flux and concentration gradient measurements at Harvard Forest Environmental Measurement Site.

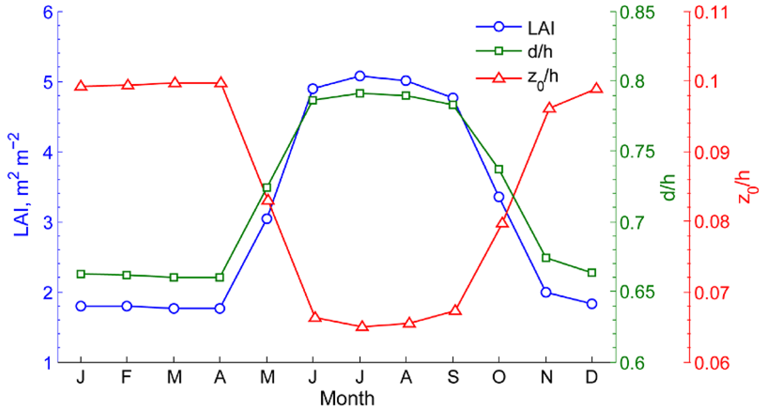

Figure 2. Monthly variation of leaf area index (LAI), the displacement height (*d*) to canopy height (*h*) ratio, and the roughness length (z_0) to canopy height ratio at Harvard Forest.

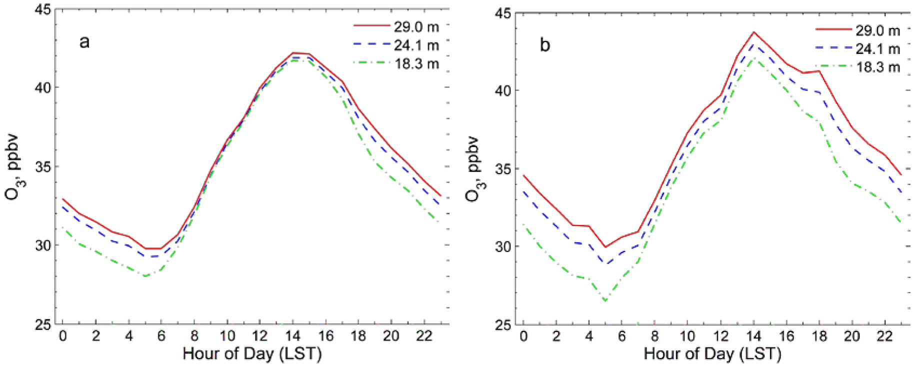

Figure 3. Mean diurnal cycles of O_3 concentration at heights of 29, 24.1, and 18.3 m a.g.l. at Harvard Forest during 1993–2000. **(a)** was derived from the original data, and **(b)** was from the data after selection.

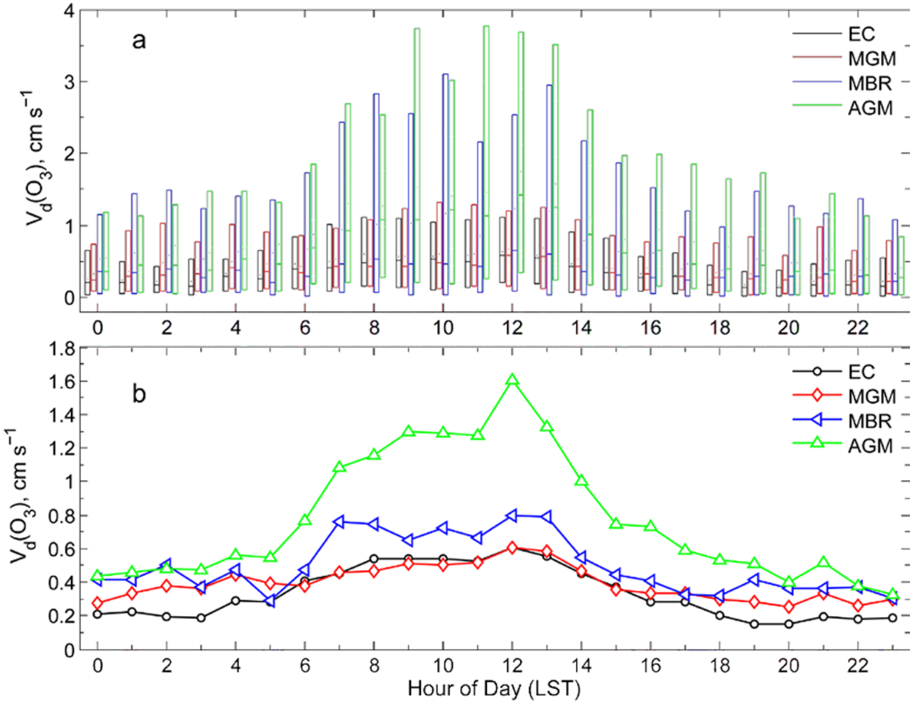

Figure 4. **(a)** The box-plot of hourly $V_d(O_3)$, and **(b)** diurnal average cycles of $V_d(O_3)$ at Harvard Forest during 1993–2000 as measured by the eddy-covariance (EC) and three gradient methods (MGM: the modified gradient method; MBR: the modified Bowen-Ratio method; AGM: the aerodynamic gradient method). In each box, the central mark is the median, and the edges of the box are the 10th and 90th percentiles. Note that the average is the arithmetical mean of data between 10th and 90th percentiles.

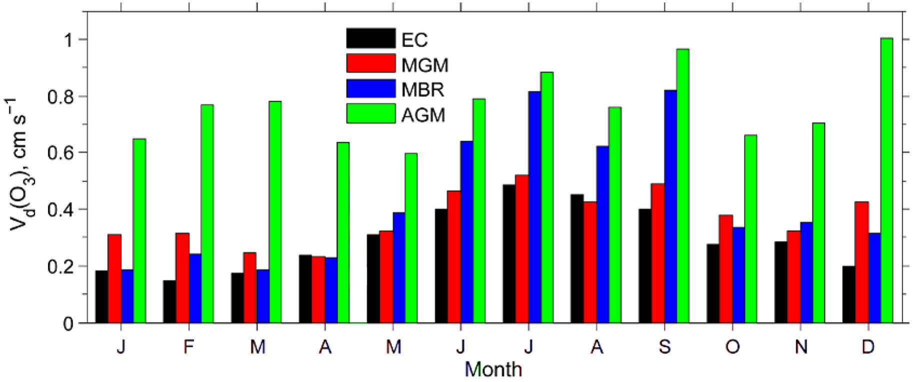

Figure 5. Monthly average of $V_d(O_3)$ at Harvard Forest during 1993–2000 as measured by the eddy-covariance (EC) and three gradient methods (MGM: the modified gradient method; MBR: the modified Bowen-Ratio method; AGM: the aerodynamic gradient method). Note that the average is the arithmetical mean of data between 10th and 90th percentiles.

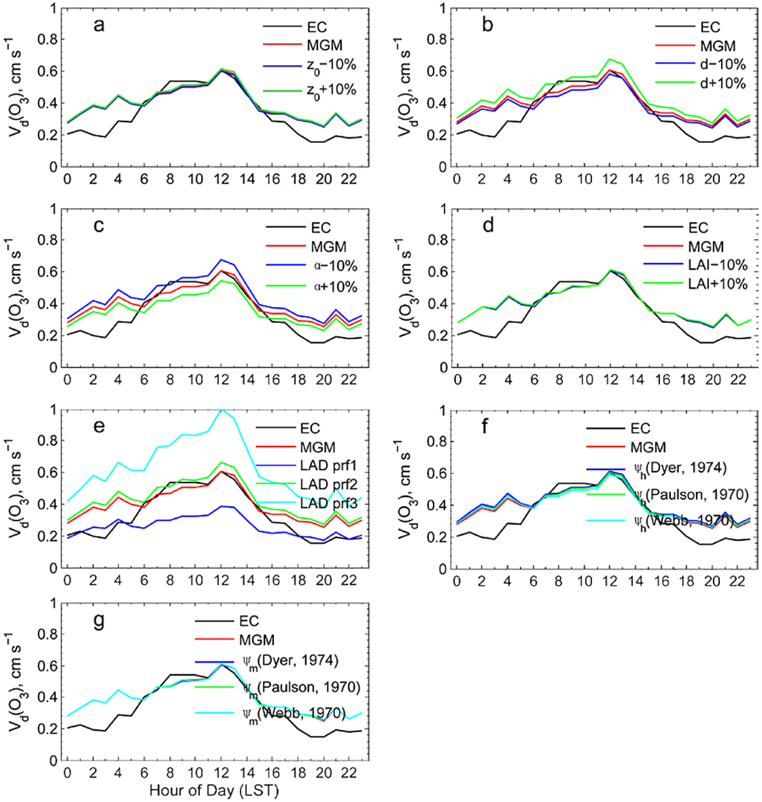

Figure 6. Diurnal average cycles of $V_d(O_3)$ over Harvard Forest during 1993–2000 by the modified gradient method (MGM) with different parameter/formula changes and compared with that by the eddy-covariance (EC) technique: **(a)** roughness length, **(b)** displacement height, **(c)** wind speed attenuation coefficient, **(d)** leaf area index, **(e)** vertical profile of leaf area density, **(f)** stability correction functions for heat, and **(g)** stability correction functions for momentum.

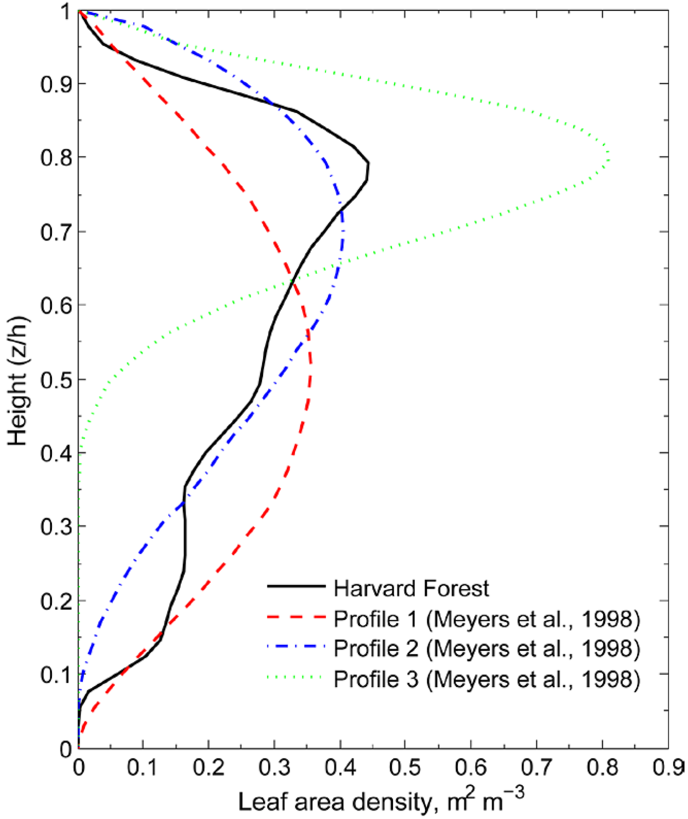

Figure 7. Vertical profiles of leaf area density in Harvard Forest and those used in sensitivity experiments.