May 21, 2015

Dear Prof. Dr. Karl,

Thank you very much for editing the paper. We have revised the paper and addressed all the comments provided by the reviewers. Our detailed replies are attached below.

For your and the reviewers' convenience to review the changes, a copy of the text with highlighted changes (from track changes) is also attached here.

We hope you and the reviewers will find the revised paper meets the standard of the journal.

Sincerely,

Zhiyong Wu and coauthors

Response to Referee #1

We greatly appreciate all the comments, which improved the paper. Our point-by-point responses are detailed below. AC – Authors Comments.

General Comments

The paper is a useful contribution to the issue of dry deposition over a forest. It describes a new method- the modified micrometeorological gradient method- which is in better agreement with eddy-covariance-EC- observations then the more traditional gradient methods.

Specific comments

On page 782, line 15, the authors make clear that the method is still based on the flux gradient theory. This remark is repeated at several places in the paper, as f.e on page 785, where its is mentioned that the flux-gradient method is questionable within the canopy. The question arises how serious this is, what is the impact of this restriction. It is recommended that the authors write some sentences about this.

AC: We have rewritten the first paragraph of section 2.4 to address this comment. It now reads "The newly proposed MGM method is also based on the flux-gradient theory (Eq. 2). It is noted that the flux-gradient theory has been long questioned within plant canopy environment due to infrequent but predominant large eddies within canopy (Wilson, 1989; Raupach, 1989). For example, Bache (1986) suggested that the flux-gradient theory was a reasonable assumption estimating wind profiles in the upper portion of canopy, but failed to reproduce the secondary wind maximum that was often observed within the trunk space of forests. It should also be noted that most of the O_3 uptake occurs in the upper layers of the canopy where most canopy leaves grow. Within these upper layers the vertical length scales of turbulence are probably smaller than the distance associated with changes in concentration and wind speed gradients (Baldocchi, 1988). Thus, the flux-gradient theory is likely applicable for estimating vertical flux distribution of air pollutants within a plant canopy, as has been used in previous studies (e.g., Baldocchi, 1988; Bash et al., 2010; Wolfe and Thornton, 2011)."

On page 785, line 13, the height-dependent Flux is introduced. What is the impact of this assumed height-dependency on the obtained results. Does this means that EC observations at the different height as they are performed now-which is 29 m, would lead to different values at f.e. 18.3 m? A similar issue arised with the remark made on page 786, line 3, where its is stated that again the constant flux approach is used. It is recommended that the authors write a short paragraph to comment on these issues.

AC: Flux above the canopy is constant (assuming no additional sink or source terms), while flux within the canopy varies with the height (due to the sink terms – O_3 uptake by leaves). The height 18.3 m is within the canopy in this case so EC measurements cannot be conducted at this height (or do not represent the total flux if measured at this height).

On page 787, formula (15), u* is introduced, without clarification. Is this the shear stress velocity at the surface, or the "effective" one at the displacement height, and how is it calculated. It is recommended that the authors clarify this issue.

AC: u_* in this study is the shear stress velocity measured at the reference height (29 m). This has been made clear in the revised paper (section 2.2).

Page 789, lines 18-21 it is discussed that in about 70 % of the observations counter gradient profiles occur. No remark is made about what is happening in these cases, which phenomenon is present, and what is the impact on the fast that in only 30 % of the cases "real" dry deposition seems to occur? It is recommended that the authors write a short paragraph on this.

AC: We have added the following explanation in the revised paper (section 3.2).
"The counter-gradient transport should be mainly due to the non-local nature of turbulent transport within canopies. Large sweep-ejection air motions associated with coherent structures that can deeply penetrate into the canopy are believed to be largely responsible for the exchange of momentum, heat and mass between air above- and within-canopy (e.g, Shaw et al., 1983; Thomas and Foken, 2007)."

Page 790, line 18-25. It is mentioned that the AGM method gives much higher values then the EC-observations. Could the authors please give a possible explanation to this finding?

AC: The aerodynamic gradient method (AGM) is not the main focus of the present study, so we simply provide some explanation based on what we found from literature. Some earlier studies have also found this method overestimated fluxes when compared with the EC method (e.g., Muller et al., 2009; Loubet et al., 2013). The large discrepancies in fluxes between those generated by AGM and EC, as found in this study, were likely cause by a combination of many different factors, such as measurements errors in both methods, selections of the R_a formula and related parameters, and the local and large scale specific meteorological, physical and chemical conditions. For example, the EC technique is found to underestimate flux during calm night-time periods (Goulden et al., 1996). O_3 fluxes measured by different EC instruments could exhibit a relative difference of up to 25% (Muller et al., 2010). AGM derives flux from the concentration gradient between two adjacent levels above the canopy, which is subject to large uncertainty due to the very small gradient and associated measurement uncertainties. AGM is subject to the drawback due to the use of empirical stability correction functions. Uncertainties in the estimation of R_a above the canopy (and thus in the flux estimation using the AGM method) can be up to 30% on long-term average (Zhang et al., 2003). Large uncertainty may also exist in the estimated parameters such as the roughness length and the displacement height which have significant effects on the calculation of R_a. Unfavorable meteorological conditions may occur, such as the large scale turbulence structures which will generate advection terms and affect the low-frequency range of the turbulent spectra. This may underestimate flux when using the EC method (Mauder and Foken, 2006).

Technical corrections

AC: All corrected.

References mentioned in this response:

Bache, D. H.: Momentum transfer to plant canopies: influence of structure and variable drag, Atmos. Environ., 20, 1369-1378, 1986.

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

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.

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, Global Change Biol., 2, 169-182, 1996.

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.

Mauder, M. and Foken, T.: Impact of post-field data processing on eddy covariance flux estimates and energy balance closure, Meteor. Z., 15, 597–609, 2006.

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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.

Shaw, R. H., Tavangar, J., and Ward, D. P.: Structure of the Reynolds stress in a canopy layer, J. Clim. Appl. Met., 22(11), 1922-1931, 1983.

Thomas, C. and Foken, T.: Flux contribution of coherent structures and its implications for the exchange of energy and matter in a tall spruce canopy, Bound.-Lay. Meteorol., 123, 317–337, 2007.

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.

Wolfe, G. M. and Thornton, J. A.: The Chemistry of Atmosphere-Forest Exchange (CAFE) Model – Part 1: Model description and characterization, Atmos. Chem. Phys., 11, 77–101,doi:10.5194/acp-11-77-2011, 2011.

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Response to Referee #3

We greatly appreciate all the comments, which improved the paper. Our point-by-point responses are detailed below. AC – Authors Comments.

The authors present a modified micrometeorological gradient method (MGM) to infer trace gas fluxes from gradients, which should overcome the problem of very small gradients above the canopy. The small gradients above canopy require high sensitivity and accuracy of the sensors when using the aerodynamic gradient method (AGM) or the modified Bowen ratio method (MBR). To increase the gradient a level below canopy top is included in the gradient calculations as the canopy is a substantial sink (or source) for many trace gases. The authors use a 7 years data series of parallel measurements of O3 fluxes measured by eddy covariance (EC) and trace gas profiles to test their method. A well-known problem for inferring fluxes within tall canopies are so called counter gradient fluxes, which means the turbulent flux is in the opposite direction than implied by the gradient. Roughly 70 % of the available data was rejected because of the occurrence of counter gradient fluxes (74 % rejected in total). For the remaining 26 % of the data points there was an overall agreement of all methods on the diurnal cycle, but flux-gradient methods gave larger values of the deposition velocity (factor ~1.2 to 2.3) than EC. Best agreement was found between EC and MGM, with the MGM derived deposition velocities being on average about 20 % larger than those derived from EC measurements.

General comments:

Deposition velocities are commonly used to parameterize deposition in models. Direct EC measurements of reactive species like O3 or often not available or just made during campaigns. Therefore, methods that infer deposition velocities from profiles, which are more often acquired by long term measurements, are a valuable contribution to atmospheric sciences. However, this method replaces the problem of the small gradients above canopy by a more complex calculation that has to deal with height dependent fluxes within the canopy. Although the method proved to give similar results as the EC-method (based on the ~ 25 % of data left after the selection process) I would recommend some further analysis before publishing. Of special interest would be an evaluation of the meteorological conditions that lead to the most or least fraction of rejected data. The authors should as well extend the discussion on the underlying dynamical processes of turbulent motion at canopy top. The occurrence of coherent structures that penetrate the canopy causes a deviation from flux-gradient relationship and counter gradient fluxes (Denmead and Bradley, 1985). Therefore, I assume that excluding counter gradient data will remove most of the periods where the transport is influenced or even dominated by coherent structures. The detection of coherent structures has been used to qualitatively describe the coupling of the different canopy layers (Thomas and Foken, 2007). Furthermore, efficient vertical trace gas transport from the forest floor throughout the canopy has been linked to coherent structures (Sörgel et al., 2011; Foken et al., 2012; Zeeman et al., 2013). I wonder if this effect will cause a bias towards lower fluxes as there might be more frequent cases with a decoupled subcanopy that otherwise contributes to the flux as well (O3 at or within the ground is zero).

AC: This comment does provide us very useful information explaining the large percentage of counter gradient data observed at this site. While a portion of the counter gradient data (especially those with small gradients) could be caused by measurement uncertainties, others were likely caused by specific meteorological conditions as suggested by this reviewer. Detailed investigation on these counter gradient data can be interesting and may generate new knowledge on the surface-layer flux exchange processes. Such a detailed analysis is outside the scope of the present study and can be done in a separate study if all the required data are available. This study focuses on developing a new method to quantify dry deposition fluxes of O_3 using gradient measurements, and for this purpose, only positive gradient data are useful. Previous studies of the local meteorology at the Harvard Forest site indicated that this site is suitable for eddy-covariance flux measurements due to a lack of anomalous flow patterns and an energy budget that is closed to within 15% (Moore et al., 1996; Goulden et al., 1996). Most of the periods associated with coherent structures should be filtered out due to omitting of counter-gradient data. Therefore, the contribution of coherent structures to the long-term averaged fluxes is expected to be small.

We have reviewed references provided by the reviewer, and provided a short discussion on this counter gradient issue in the revised paper. It reads: “The counter-gradient transport should be mainly due to the non-local nature of turbulent transport within canopies. Large sweep-ejection air motions associated with coherent structures that can deeply penetrate into the canopy are believed to be largely responsible for the exchange of momentum, heat and mass between air above- and within-canopy (e.g, Shaw et al., 1983; Thomas and Foken, 2007). ”

Are the deposition velocities scaled to the same O3 concentration (reference height)? This would mean that the fluxes are overestimated by all gradient methods. Any reasons for this behavior?

AC: Yes, they are all scaled to the reference height at 29 m, as shown in Eq. 19. We have provided some speculations in our responses to Reviewer #1 on a similar comment. Here we’d like to add a few more points. The stability correction functions used in the gradient methods (AGM and MGM) are subject to large uncertainties under stable conditions (Högström, 1988). MBR assumes equality of eddy diffusivity *k* between scalars. However, Loubet et al. (2013) found that the eddy diffusivities for O_3 were just around half of those for sensible heat, CO_2 and H_2O. This might explain the overestimation of $V_d(O_3)$ by MBR in this study, but more field studies are needed to verify this.

The authors report that the model (with a given LAI-profile) is most sensitive to changes in the wind speed attenuation coefficient and displacement height (d). As the roughness elements (tree-crowns) are inhomogeneously distributed, do you expect a dependence of these values on wind direction? Furthermore, d has been reported to be stability dependent as well (Zilitinkevich et al., 2008; Zhou et al., 2012). Might this be a reason why MGM overestimates fluxes during night?

AC: We determined the wind attenuation coefficient using noon-period wind profile measured during a short campaign in July of 1996. The southwestern winds dominated during the campaign. It is hard to interpret the dependence of wind speed attenuation coefficient on wind direction due to the limited data points from different wind directions. However, the coverage of the forest around the HFEMS site is fairy homogeneous (Moody et al., 1998; Min and Lin, 2006) and the influence of wind direction on wind attenuation coefficient or displacement height is expected to be minimal.

As proposed by Zilitinkevich et al. (2008), displacement height (*d*) is greater under stable stratification than under neutral-stability condition. But our sensitivity tests show that the MGM $V_d(O_3)$ increased when *d* increased (Fig. 6 and Table 2 in the manuscript). Therefore, the possible underestimation of *d* at night could not explain the overestimation by MGM. This discrepancy could be due to the fact that nocturnal conditions affect both EC and gradient measurements as discussed in the manuscript.

Specific comments:

P785 L9: As this is a basic assumption one should mention here that Baldocci (1988) says that based on the work of Bache (Bache, 1986), his measured SO2 profile and the more theoretical considerations of Corrsin (1974) he"…suggests that 'K-theory' models may be valid for estimating SO2 exchange in tall vegetation because the length scales of the turbulence are probably smaller than the distances associated with changes in the concentration and wind speed gradients." This means, that this assumption is not proven it's just plausible.

AC: We have rewritten the first paragraph of section 2.4 to address this comment. It now reads "The newly proposed MGM method is also based on the flux-gradient theory (Eq. 2). It is noted that the flux-gradient theory has been long questioned within plant canopy environment due to infrequent but predominant large eddies within canopy (Wilson, 1989; Raupach, 1989). For example, Bache (1986) suggested that the flux-gradient theory was a reasonable assumption estimating wind profiles in the upper portion of canopy, but failed to reproduce the secondary wind maximum that was often observed within the trunk space of forests. It should also be noted that most of the O_3 uptake occurs in the upper layers of the canopy where most canopy leaves grow. Within these upper layers the vertical length scales of turbulence are probably smaller than the distance associated with changes in concentration and wind speed gradients (Baldocchi, 1988). Thus, the flux-gradient theory is likely applicable to estimating vertical flux distribution of air pollutants within a plant canopy, as has been used in previous studies (e.g., Baldocchi, 1988; Bash et al., 2010; Wolfe and Thornton, 2011)."

P790 L 5: From Fig. 3 it seems that photochemical O3 formation is still dominant until the early afternoon (O3 maximum). Furthermore, what about reactions that eliminate O3. I.e. reaction with NO and unsaturated VOCs.

AC: Currently we don't have enough data (e.g., speciated VOCs measurements) to estimate the reaction rates of O_3 production/consumption at the Harvard Forest site. We reviewed literature and found that many studies (e.g., De Arellano and Duynkerke, 1992; Duyzer et al., 1997; Gao et al., 1991; Padro et al., 1998; Stella et al., 2012) showed that the effects of chemistry on O_3 flux divergence in the near surface were generally small, likely because the chemical reactions for O_3 have larger time scales than the turbulent transport. On the other hand, the effective turbulent exchange could be a reason for the small O_3 gradient in the morning as stated in an early study (Sörgel et al., 2011), which showed that a complete coupling of air within- and above-canopy was usually achieved in early morning. A statement on this has been added in the revised paper in section 3.2.

References mentioned in this response:

Bache, D. H.: Momentum transfer to plant canopies: influence of structure and variable drag, Atmos. Environ., 20, 1369-1378, 1986.

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De Arellano, J. V. G. and Duynkerke, P. G.: Influence of chemistry on the flux-gradient relationships for the NO-O_3-NO_2 system, Bound. Lay. Meteorol., 61, 375–387, 1992.

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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.

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Shaw, R. H., Tavangar, J., and Ward, D. P.: Structure of the Reynolds stress in a canopy layer, J. Clim. Appl. Met., 22(11), 1922-1931, 1983.

Sörgel, M., Trebs, I., Serafimovich, A., Moravek, A., Held, A., and Zetzsch, C.: Simultaneous HONO measurements in and above a forest canopy: influence of turbulent exchange on mixing ratio differences, Atmos. Chem. Phys., 11, 841–855, doi:10.5194/acp-11-841-2011,15 2011.

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Thomas, C. and Foken, T.: Flux contribution of coherent structures and its implications for the exchange of energy and matter in a tall spruce canopy, Boundary-Layer Meteorol., 123, 317–337, 2007.

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.

Wolfe, G. M. and Thornton, J. A.: The Chemistry of Atmosphere-Forest Exchange (CAFE) Model – Part 1: Model description and characterization, Atmos. Chem. Phys., 11, 77–101,doi:10.5194/acp-11-77-2011, 2011.

Zilitinkevich, S. S., Mammarella, I., Baklanov, A. A., and Joffre, S. M.: The effect of stratification on the aerodynamic roughness length and displacement height. Bound.-Lay. Meteorol., 129(2), 179-190, 2008.

Response to Thomas Foken

We greatly appreciate Thomas Foken for providing the comments which have helped us to improve the paper. Our point-by-point responses are detailed below. AC – Authors Comments.

The measurement of deposition fluxes above tall vegetation is a never ending story because of many challenges. Very important is the small gradient of temperature and trace gases above the canopy, which is often lower than the detection limit of the sensors/analyzers (Foken, 2008, p. 135). The authors try to overcome this problem by using a gradient between a level above the canopy and one within the canopy, with a significant increasing of the gradient. Unfortunately, they do not discuss the influence of relevant processes at the top of the canopy on the new proposed method, like roughness sublayer or mixing layer (Garratt, 1978; Finnigan, 2000; Harman and Finnigan, 2007, 2008) (Raupach et al., 1996), decoupling (Thomas and Foken, 2007a), coherent structures (Collineau and Brunet, 1993a, b; Thomas and Foken, 2007b), scalar similarity (Ruppert et al., 2006), and reactions. Some of the effects may not be relevant due to the selection of only 26 % of the data set for the analysis. Because the abovementioned processes have a daily and annual cycle, it would be interesting to see a daily and annual cycle of the availability of the data. I assume that only situations with moderate and high wind velocities and a good coupling of the atmosphere with the upper canopy layer were used.

AC: The issues raised here and references provided do help us better understand the complex processes involved in the air-surface flux exchange of trace pollutants above tall canopies. As we have responded to Referee #3, detailed investigation on all the issues would require substantial additional efforts which can only be done in future studies. The present study focuses on the development of a new gradient method and thus only chooses data that fits such an application. As also mentioned by this reviewer, only using 26% selected data likely avoids many of the non-ideal conditions affecting the suitability of the modified gradient method. In the revised paper, we have added some brief discussions as detailed in our response to Referee #3.

Per the reviewer's request, we have also provided below (Figure 1) the diurnal and seasonal patterns of data points available for analysis. There are about 75-155 data points in each hour with two peaks in the early morning (7-8 LST) and the late afternoon (14-16 LST). The number of data points available in each month indicated a significant season trend with the most data points in summer (~400) and the least in winter (~50). This is primarily due to the data availability in the original data set (better data coverage in summer). Apparently, both the original data coverage and the non-ideal conditions affected the number of data points chosen for the final analysis. More detailed analysis is needed in order to generate any meaning results so we chose not to include such information in the revised paper.

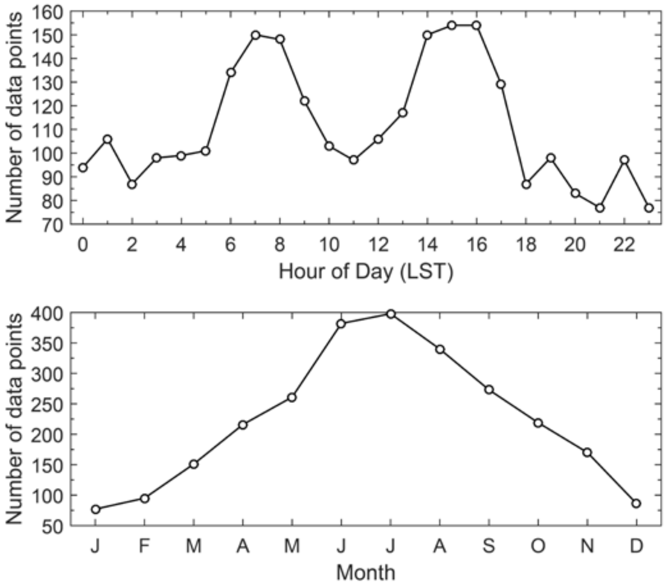

Figure 1. Hourly and monthly number of data points available for analysis.

The most relevant problem is the calculation of the aerodynamic resistance in Eq. 5. This leads to an overestimation of the deposition velocity by the aerodynamic gradient method (AGM). But this aerodynamic resistance is also used in the proposed micrometeorological gradient method (MGM), Eq. 11. I assume that z2 is equal to h, because no other measurements were available. It is extremely difficult to make exact measurements at the top of the canopy because of the extreme gradient at this height, the heterogeneity of the forest and a possible dependence on the wind direction and the strong influence of the roughness sublayer (mixing layer). The authors encountered this problem through the strong influence of the wind velocity on the results, because the wind field penetrates more or less into the forest and the level with the extreme gradient is either a little bit above or below the top of the canopy.

AC: In Eq. 11, *h* is the height of canopy, which is smaller than z_2 in Eq. 3-5 since z_2 is the reference height at a level above the canopy. There are two unknown variables both in Eq. 11 and 9, i.e., C_h and F. By combing them, C_h and F can be both resolved.

It is not true that the AGM always overestimates the deposition velocity. If you measure not at the top of the canopy but at two levels at certain distances from the top, and apply a roughness sublayer correction function (Garratt, 1978), you can measure fluxes accurately (Wolff et al., 2010a; Wolff et al., 2010b; Foken et al., 2012). Unfortunately, this method is limited due to the accuracy of the gas analyzer, which is probably not good enough for ozone.

AC: We agree that not every study shows AGM overestimates flux. Some studies (Keronen et al., 2003; Stella et al., 2012) showed that $V_d(O_3)$ by the AGM and EC methods generally agreed well, while the other studies (Muller et al., 2009; Loubet et al., 2013) found a significant overestimation by the AGM method, consistent to what we found in this study. We have provided a brief summary of these earlier studies in the revised paper.

Because the aerodynamic resistance in Eq. 5 – and therefore also in Eq. 11 – is too small (flux and deposition velocity are too large), this must be compensated for by the aerodynamic resistance in the layer from h to z3, Eq. 10, so that the sum of both resistances in Eq. 12 is again accurate and a deposition velocity (flux) can be calculated in a good agreement with the eddy-covariance data. In other words, the calculation of the integral in Eq. 10 must be wrong (too large resistance), even when the Eqs. 13 ff appear to be in a good agreement with the theory. What was the tuning parameter of your model?

AC: We determined most of the parameters (e.g., leaf area density, roughness length, displacement height, wind attenuation coefficient) using measurements collected at the Harvard Forest and some parameters were chosen from literature (e.g., Prandtl/Schmidt number). Due to the limitation of available measurements, some parameters were derived from short-term measurements but applied to the calculation for long-term flux. Although there exist uncertainties, these parameters should be within a reasonable range. In section 4.2, we conducted the sensitivity tests to identify the key parameters/formulas and assessed the effects of parameter uncertainties on the model results.

The logic provided here seems to be right. However, if you take into account the following factors, the conclusion is not necessarily accurate. These factors include (1) the gradient between the two levels both above the canopy is much smaller than that between the two levels with one level inside the canopy, and (2) the flux above the canopy is constant (at least in theory) while the flux just below the canopy decreases rapidly with decreasing height. Thus, in the original AGM, underestimation of the aerodynamic resistance (R_a) overestimates deposition velocity (V_d). In the MGM, it is the term that below the canopy (Eqs. 9 and 10) dominates the final V_d value. The underestimation in R_a (Eq. 5) should only contribute a small percentage in the overestimation of the final V_d. Thus, in the MGM method, Eq. 10 is not necessarily wrong. The reviewer's logic actually helped us explain why the MGM still slightly overestimate V_d (especially during night time when R_a value is large and play a more important role), which is likely caused by the underestimation of R_a (Eq. 5). In other words, if Eq. 10 gives an accurate estimation, then the underestimation of R_a in Eq. 5 should give a small overestimation in the final V_d in the MGM method, as is the case shown in our results. To confirm this, we conducted a sensitivity test by increasing R_a by a factor of 1.5 in both the AGM and the MGM methods (Figure 2). We can see that while V_d in AGM changes dramatically, V_d in MGM only changed slightly, which confirmed our argument above. We, however, do agree that if an existing R_a formula gives larger R_a values, then (Eqs. 9 and 10) can be chosen slightly smaller values. We need to keep in mind that all chosen parameters/formulas need to be based on available measurements and within reasonable ranges. We recently applied this MGM method to a five-year O_3 and SO_2 gradient data collected at our Borden monitoring site (Ontario) and we generated very reasonable V_d values for both SO_2 and O_3 (to be presented in a separate study), which demonstrates the applicability of this new method.

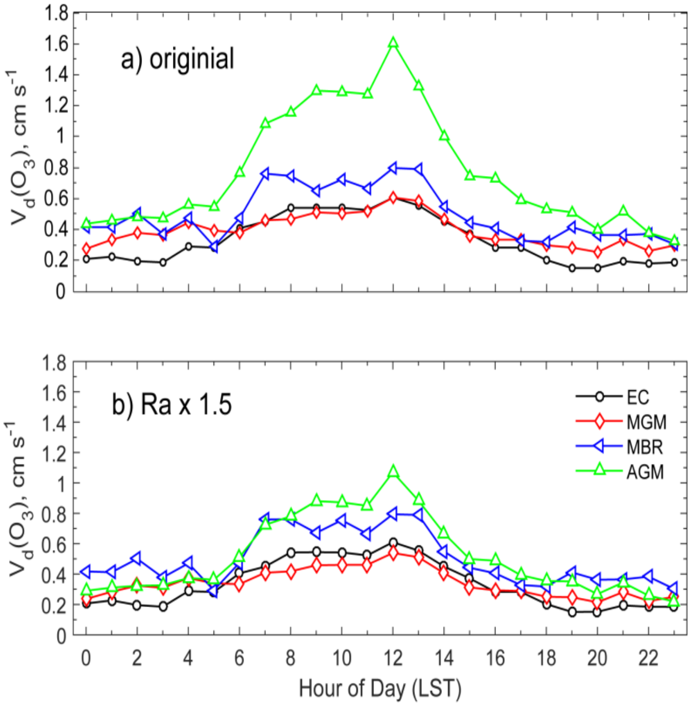

Figure 2. Sensitivity test using 1.5 times of R_a to replace R_a.

By the way, the applied universal function by Businger et al. (1971) in the modified form by Högström (1988) already includes a turbulent Prandtl number for the sensible heat flux ,or a turbulent Schmidt number for trace gas fluxes (Foken, 2006). On the other hand, you use a turbulent Schmidt number of 0.8 (p. 786, line 9); make sure that you did not use the turbulent Schmidt number twice.

AC: No, the turbulent Schmidt number was not used twice. The universal function for trace gas was applied in the calculation of aerodynamic resistance above canopy ($R_a(z_1{:}h)$) while the turbulent Schmidt number of 0.8 was applied in the calculation of aerodynamic resistance below canopy ($R_a(h{:}z_3)$).

The modified Bowen ratio method (MBR) was not the main topic of the paper, but it is important to show a good scalar similarity between ozone and the proxy (carbon dioxide). This is not trivial, because the ozone flux is influenced mainly in the morning by high reactions with NO, emitted during the night, and the assimilation is probably limited in the afternoon (Ruppert et al., 2006).

AC: We reviewed literature and found that many studies (e.g., De Arellano and Duynkerke, 1992; Duyzer et al., 1997; Gao et al., 1991; Padro et al., 1998; Stella et al., 2012) showed that the effects of chemistry on O_3 flux divergence in the near surface were generally small, likely because the chemical reactions for O_3 have larger time scales than the turbulent transport (which is likely due to the much higher O_3 concentrations compared to those of NO_x, Padro et al., 1998). Thus, the influence of chemical reactions on the similarity between O_3 and CO_2 is expected to be small. Of course many other factors may influence this similarity since different scalars have different source and sink terms. Detailed discussion on this topic is out of the scope of this study and existing literature certainly has substantial information on this topic.

For the final publication you should show which phenomena at the top of the forest canopy you excluded due to the data selection. The influence of the roughness sublayer should be discussed and the main point is: Because Ra (z1:h) is obviously too small, how have you modified Ra(h:z3) so that Ra(z1:h) + (Ra(h:z3) is again accurate?

AC: See our response and the figure provided to a comment above. While we agree that there is a possibility that R_a is an underestimation, measurement uncertainties in concentration gradients could also cause such big discrepancies between AGM and EC due to the very small gradients. This possibility is also supported by the fact that the MBR method also overestimates fluxes taking EC measurement as a standard.

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

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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; Wu et al., 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 product~~ion~~ 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 field ~~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 Section 2, the measurement data in Section 3, comparison results and sensitivity tests in Section 4, and major conclusions and recommendations in Section 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*):

$$F = \overline{w'c'} \qquad (1)$$

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:

$$F = -K_c(z)\,dC/dz \tag{2}$$

where K_c is the eddy diffusivity for the gas, and dC/dz 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

$$R_a(z_1:z_2) = \int_{z_2}^{z_1} dz/K_c(z) \tag{3}$$

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:

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

where 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 $\left(u_* \equiv \left(-\overline{u'w'}\right)^{1/2}\right)$ measured at the reference height, 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:

$$K_c = K_{co_2} = -F_{co_2}\,\Delta z / \Delta C\left(CO_2\right) \qquad (6)$$

where K_{co_2} is the eddy diffusivity of CO_2, F_{co_2} is the eddy-covariance flux of CO_2, $\Delta C\left(CO_2\right)$ is the concentration gradient of CO_2 over the same height interval as $\Delta C\left(O_3\right)$, and Δz is the height interval of concentration measurements.

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

$$F = F_{co_2}\,\Delta C\left(O_3\right) / \Delta C\left(CO_2\right) \qquad (7)$$

2.4. Modified gradient method (MGM)

The newly proposed MGM method is also based on the flux-gradient theory (Eq. 2). ~~While~~It is noted that 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).~~,~~ For example, Bache (1986) suggested that the flux-gradient theory was a reasonable assumption estimating wind profiles in the upper portion of canopy, but failed to reproduce the secondary wind maximum that was often observed within the trunk space of forests. ~~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~~ It should also be noted that most of the O_3 uptake occurs in the upper layers of the canopy where most canopy leaves grow. Within these upper layers~~and~~ the vertical length scales of turbulence are probably smaller than the distance associated with changes in ~~the~~ concentration and wind speed gradients (Baldocchi, 1988). Thus, the flux-gradient theory ~~approach~~ is likely applicable~~has been used~~ ~~to~~ for estimating~~e the~~ vertical flux distribution~~profile~~ of air pollutants within a plant canopy, as has been used in previous studies (e.g., Baldocchi, 1988; Bash et al., 2010; Wolfe and Thornton, 2011).

~~Similar to the~~Applying the flux-gradient theory within the canopy~~applied in the constant flux layer above canopy~~, a height-dependent flux (*F(z)*) can then be calculated~~within canopy is computed~~ as:

$$F(z) = -K_c(z)\frac{dC}{dz} \tag{8}$$

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

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

where C_h and C_3 are the concentrations at canopy top (h) and the height of z_3 ($z_3<h$), respectively. $R_a(h:z_3)$ is related to K_c as

$$R_a(h:z_3) = \int_{z_3}^{h} dz/K_c(z) \tag{10}$$

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:

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

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

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

$R_a(z_1 : h)$ is calculated using~~by~~ Eq. (5). $R_a(h : z_3)$ is ~~computed as the~~integrated vertically between the two heights~~integration of~~ within the canopy using ~~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

$$K_m(z) = \frac{\int_0^z C_m(z)\, a(z)\, u(z)^2\, dz}{du(z)/dz} \tag{13}$$

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):

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

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

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

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

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

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:

$$u_h = u(z_1)\frac{\ln(h-d) - \ln(z_0) + \psi_m\left[(h-d)/L\right] - \psi_m\left[z_0/L\right]}{\ln(z_1-d) - \ln(z_0) + \psi_m\left[(z_1-d)/L\right] - \psi_m\left[z_0/L\right]} \tag{18}$$

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

$$V_d = -F / C(z_1) \tag{19}$$

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 ~5.0 $m^2 m^{-2}$ 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 AGL 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). As ~~T~~the measurements during January and February were not available, these ~~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):

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

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

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 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). The counter-gradient transport should be mainly due to the non-local nature of turbulent transport within canopies. Large sweep-ejection air motions associated with coherent structures that can deeply penetrate into the canopy are believed to be largely responsible for the exchange of momentum, heat and mass between air above- and within-canopy (e.g, Shaw et al., 1983; Thomas and Foken, 2007). 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.

Fig. 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 LST) compared to the other periods of the day. In the morning, the most effective turbulent exchange between the air above- and within-canopy would substantially reduce the gradients (Sörgel et al., 2011). It is worth to mention that many earlier studies suggested that the effects of chemistry on O_3 flux divergence in the near surface were generally small, likely because the chemical reactions for O_3 have larger time scales than the turbulent transport (e.g., Gao et al., 1991; De Arellano and Duynkerke, 1992; Duyzer et al., 1997; Padro et al., 1998; Stella et al., 2012).~~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 ppbv 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, 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 U.S. grassland site.

Fig. 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 cm s^{-1} on average during night and reached a daily maximum of 0.5 cm s^{-1} around noon. The $V_d(O_3)$ by the MBR and AGM methods reached around 0.8 and 1.3 cm s^{-1} during the daytime, respectively and remained about 0.4 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 (AGM and MGM) are subject to large uncertainties under stable conditions (Högström, 1988).

The very large differences in $V_d(O_3)$ between the AGM and EC methods should be caused by a combination of various factors. As can be seen from Eq. (4), any underestimation in the calculation of aerodynamic resistance (R_a) would directly transfer to the overestimation of V_d. Uncertainties in R_a from using different formulas are generally on the order of 30% over a whole canopy (Zhang et al., 2003). In the case of Eq. (4), uncertainties can be larger than 30% if other uncertainties from the related parameters are larger. The potential underestimation in R_a (Eq. 4) also explains the small overestimation in V_d from the MGM method, in which the same R_a formula is used, although plays a second role. Measurement uncertainties in concentration gradients could also cause big discrepancies between the AGM and EC methods, especially under small gradient conditions. This is supported by the finding that the MBR method also overestimated V_d when compared with the EC measurements.

As shown in Fig. 5, the EC $V_d(O_3)$ exhibited a significant seasonal pattern with peak values in summer (~0.5 cm s^{-1}) and small values in winter (0.15-0.28 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 Section 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, calculations~~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).

Fig. 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). Fig. 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.

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Figure Captions

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

Fig. 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.

Fig. 3. Mean diurnal cycles of O_3 concentration at heights of 29, 24.1, and 18.3 m above ground level at Harvard Forest during 1993-2000. (a) was derived from the original data, and (b) was from the data after selection.

Fig. 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 90 th percentiles.

Fig. 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

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Fig. 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.

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

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
90 th Percentile	0.83	0.96	1.86	2.28
Mean[a]	0.34	0.40	0.49	0.77

[a] the arithmetical mean of data between 10th and 90 th percentiles

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

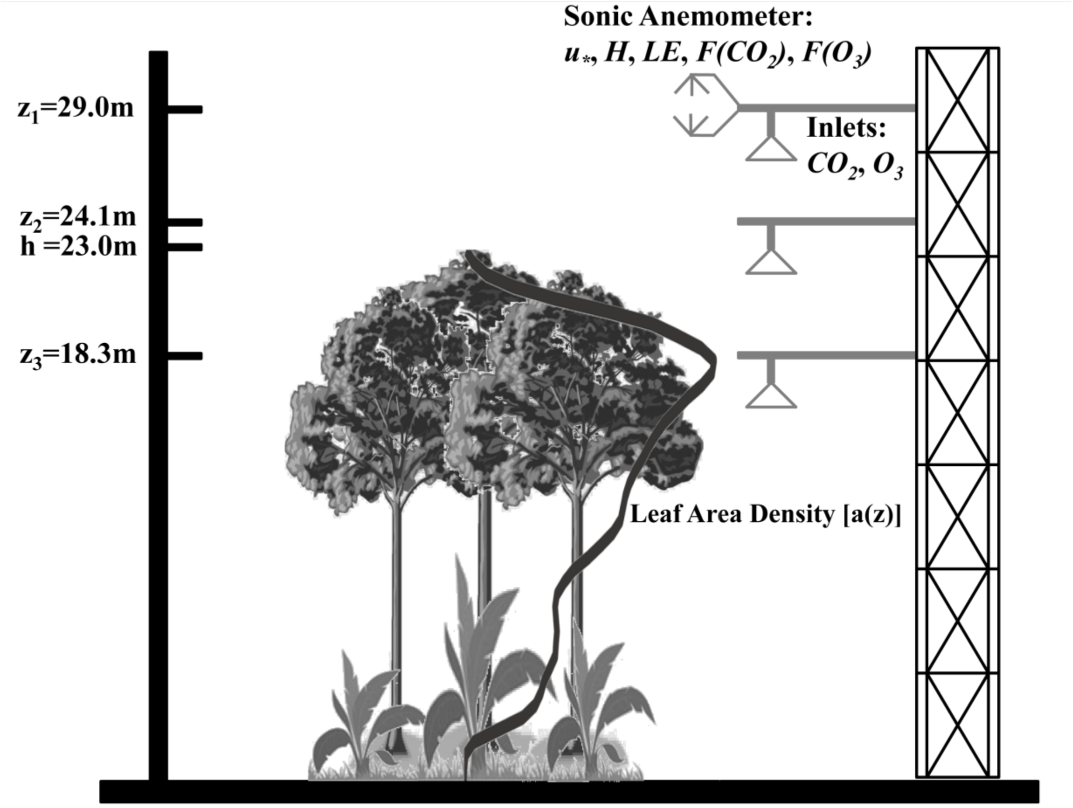
	z_0		d		α		LAI		LAD[b]			Ψ_h[c]			Ψ_m[c]		
	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	Prf 1	Prf 2	Prf 3	D74	P70	W70	D74	P70	W70
Median	-1.1	1.1	-4.8	10.8	10.1	-9.3	-0.6	0.5	-34.4	8.4	57.4	3.1	1.7	0.5	0.2	0.08	0.06
Mean[d]	-1.0	1.1	-4.7	10.4	10.2	-9.6	-0.6	0.5	-34.5	8.4	58.5	3.1	1.4	-0.01	0.1	0.02	-0.01

[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 90 th percentiles



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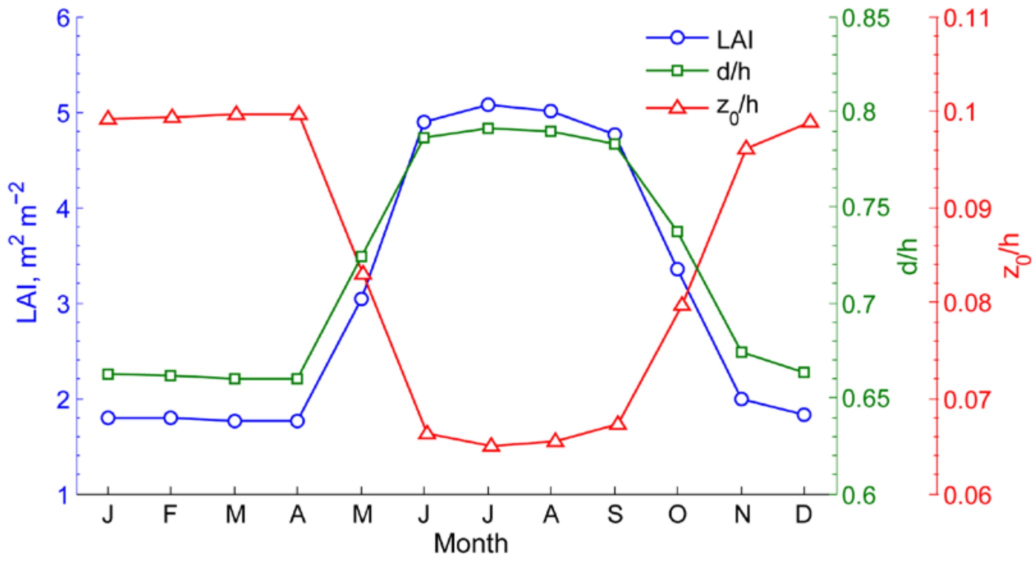

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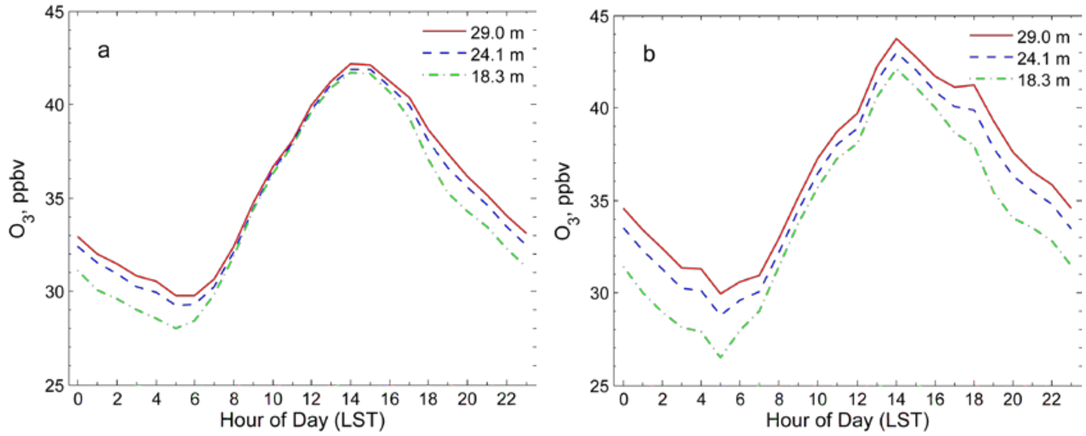

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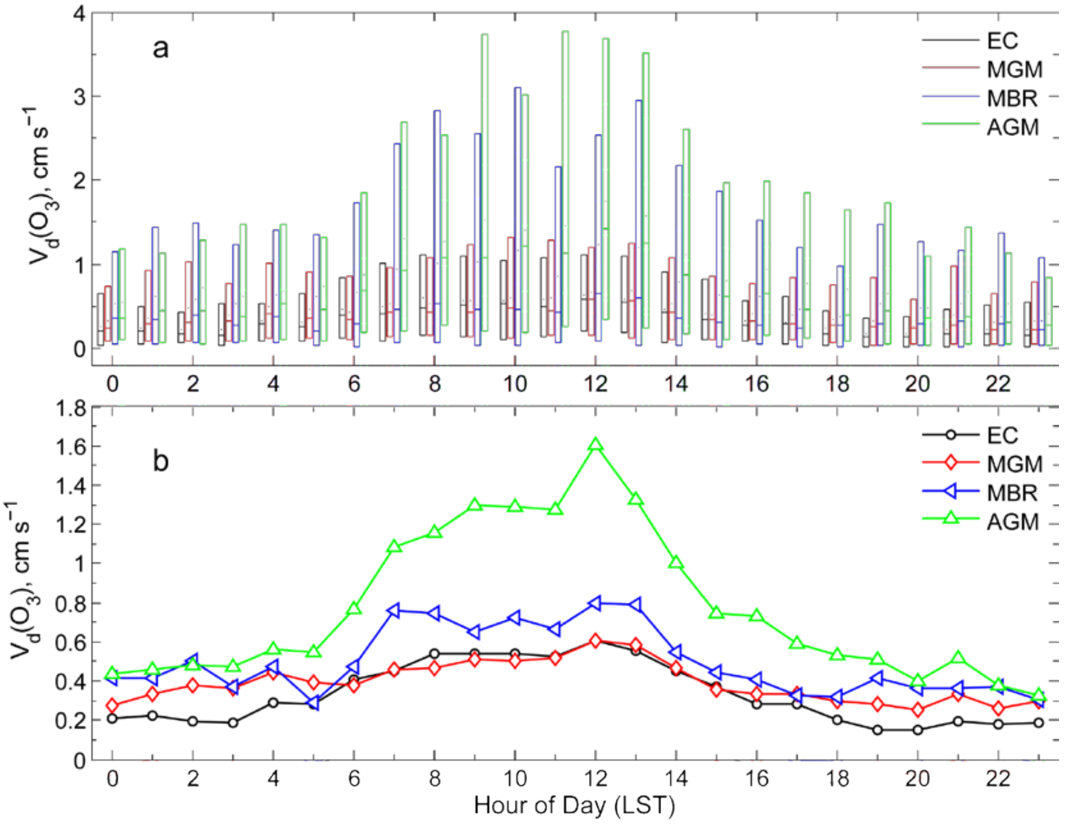

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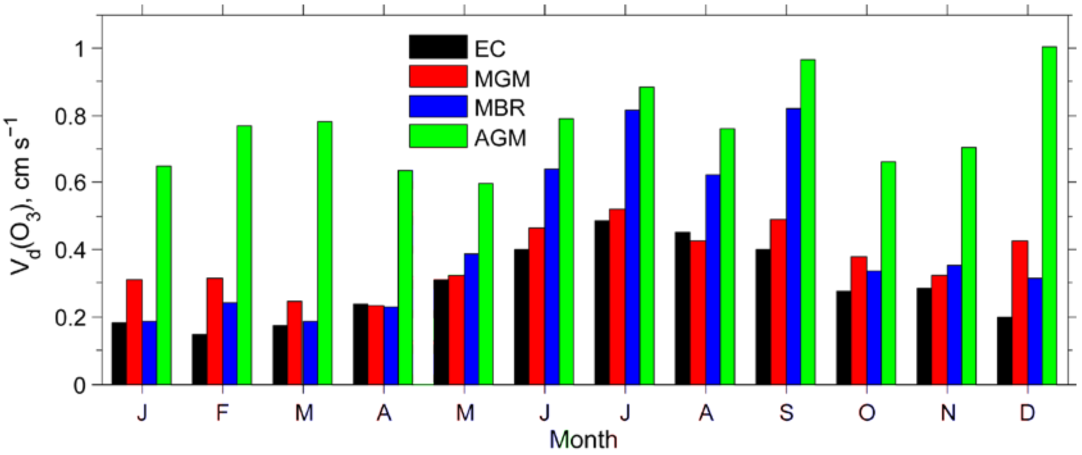

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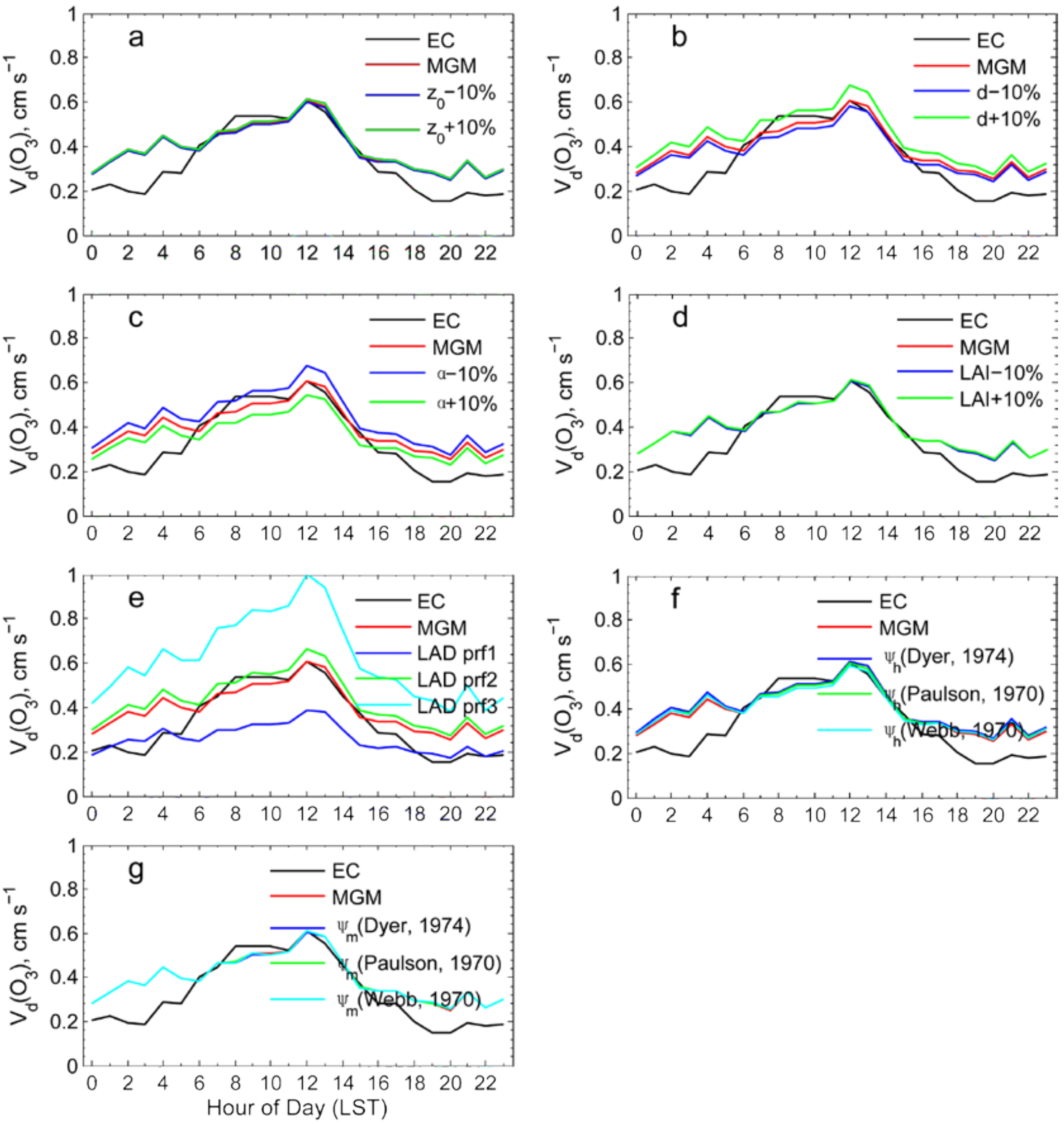

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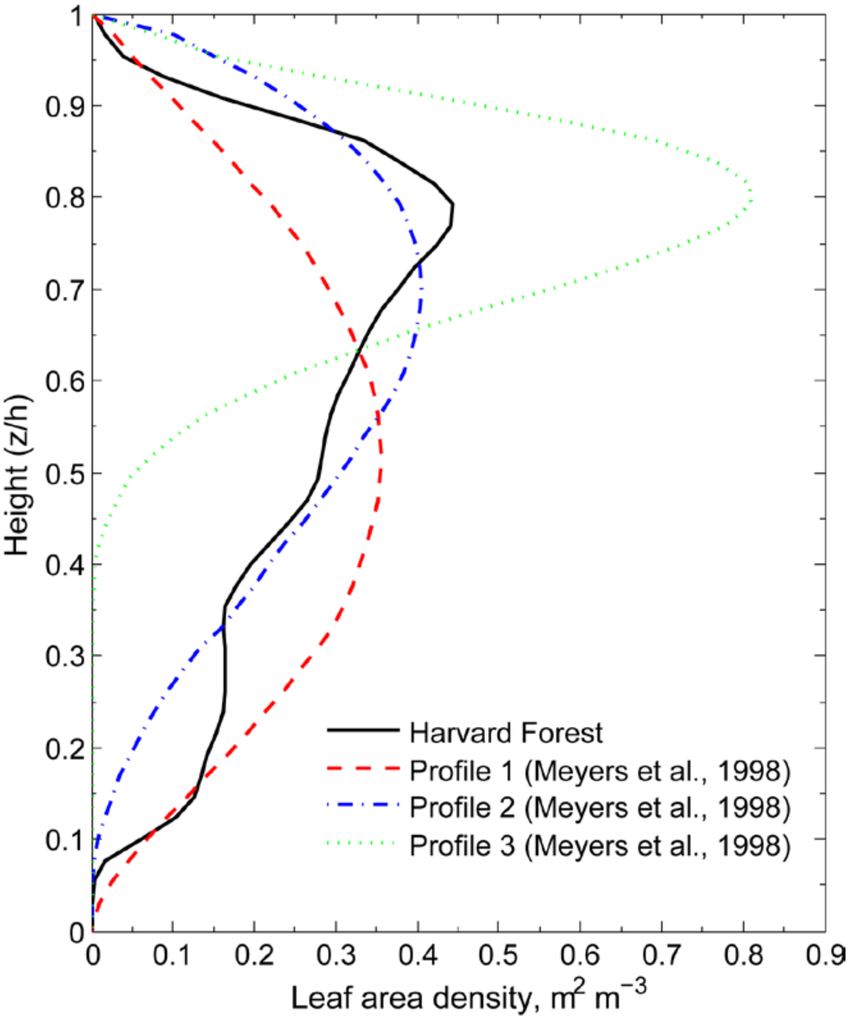

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