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.

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