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Interactive comment on "Application of thermal dissociation-laser induced fluorescence (TD-LIF) to measurement of HNO_3, Σalkylnitrates, Σperoxy nitrates, and NO_2 fluxes using eddy covariance" *by* D. K. Farmer et al.

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The analytical technique presented in this paper is very impressive. It promises a much improved assessment of speciated reactive nitrogen fluxes by Eddy Correlation approaches. The most striking feature is the clear diurnal pattern of the emission fluxes of "total HNO_3" in summer being equal to or even larger than the other three fluxes in absolute terms. We would like to comment on the presented flux errors and have some reservations about the plausibility of the resulting fluxes.

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Fluxes of ΣPAN's, ΣAN and HNO_3 are always calculated as differences between two fluxes of adjacent channels. Considering that channel 3 represents the sum of NO_2 +ΣPAN + ΣAN fluxes, figure 4 indicates that the flux recorded on the third channel (330°C) is close to zero during a large part of the day. For such cases, it is very difficult to determine a true flux, because the covariance function may not show a clear maximum and a safe lag determination is therefore not possible. Figure 3 shows an example of a covariance function of the 550°C channel with a clear downward or deposition flux. The curve is in general a mirror image of the covariance function of the heat flux, but there is one striking difference in the function of the TD-LIF channel. Superimposed on this curve are variations in the order of 20 to 30% of the maximum of the absolute value of the covariance function. As this fluctuation appears over the whole covariance function, it is probable that it also contributes at the maximum. We therefore think that this fluctuation is a more realistic indication of the precision of the flux than the values given in table 1 that have been determined from zero air analysis and theoretical considerations see also (Wienhold et al., 1996; Wienhold et al., 1994). Unfortunately the shown example falls into the transition period from emission to uptake fluxes and seems not to be representative for the typical diurnal pattern presented in Figures 4 and 9. To investigate whether advection effects or even potential instrumental artifacts influence the flux data we suggest the comparison of the cumulative cospectra of the four channels (the ogives).

We have difficulties to understand the systematic daytime emission fluxes of HNO_3 from a theoretical point of view. The authors attribute the observed HNO_3 fluxes to a production within the canopy, caused by a fast conversion of emitted NO from the soil to HNO_3. The Blodgett forest is characterized by a rather low tree density and a tree height around 9 meters. The characteristic time scale for daytime for the air exchange within the canopy will most likely be in the order of 100 to 200 sec (Holzinger et al., 2005). With a simple back on the envelope calculation we can estimate the ratio of expected NO_2 to HNO_3 fluxes caused by emission of soil NO and subsequent oxidation within the canopy. We assume that the chemical lifetime of NO_2 is determined by the OH + NO_2 reaction, thus considering this as the only net sink reaction for NO_2. With an OH radical concentration of 3*10^7 molecules cm^{-3} (a rather high value, thus probably an upper limit guess) the half-life period of NO_2 then becomes approx. 1900 sec. (We used a value of 1.2*$10^{-11}cm^3$ $molecules^{-1}$ s^{-1} (Atkinson et al., 2004) for the reaction constant OH + NO_2 -> HNO_3). Since the chemical lifetime is 10-20 times longer than the turbulent exchange scale, roughly 5-10% of NO_2 is converted to HNO_3. We would therefore expect a ratio of HNO_3 to NO_2 fluxes in the order of these 5-10%. This is an upper limit estimate of expected EC fluxes for two reasons: 1) The assumed OH concentration is rather high. 2) EC techniques measure net fluxes and deposition of HNO_3 is higher than that of NO_2 (similar concentrations of NO_2 and HNO_3 were observed during daytime and surface resistance of HNO_3 is lower). The ratio of HNO_3 to NO_2 net fluxes would therefore even be lower.

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