

Interactive comment on “Application of thermal dissociation-laser induced fluorescence (TD-LIF) to measurement of HNO_3 , Σ alkylnitrates, Σ peroxy nitrates, and NO_2 fluxes using eddy covariance” by D. K. Farmer et al.

Anonymous Referee #2

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1 General comments

The paper gives a very detailed account on the application of TD-LIF in eddy covariance flux measurements of nitrogen oxides. The topic is certainly of relevance to Atmospheric Chemistry and Physics. The principle of analysis is clearly described and the paper includes a detailed analysis of detection limits and uncertainties in flux determinations of the different nitrogen species. There is also a short account of the actual

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flux measurements over a pine plantation. The fluxes show quite interesting patterns, but maybe a more detailed account of the measurements (as planned by the authors) is necessary to really evaluate the significance of these results.

2 Specific comments

p.2931, l.9+l.23: What is the exact distance between the TD-LIF inlet and the sonic (20cm or 30cm)? A drawing of the full setup with a detailed drawing of the inlet and tubing system with dimensions and flow rates would be very useful.

p.2934, l.20: The method of determining the time lag by finding a peak in the covariance is well established. However, examining fig. 3, it seems to be quite difficult to determine the correct lag because the curve for $\sum \text{NO}_{yi}$ is quite noisy. This is normally the case when the fluxes are very low often due to low turbulence. I wonder whether the example shown is the best, or it is just typical. A good way of determining the time lag is to find cases with a high flux where the lag is well defined. Together with other knowledge such as tube flow rate and length and other delays a proper time lag interval can then be defined. At low fluxes it might be impossible to find a maximum within the given interval and a fixed lag can be applied instead. Was a common time lag calculated for the fluxes, or was it calculated for the four individual channels?

p.2938, l.1: I wonder whether the underestimation of flux due to sensor separation isn't already taken into account by the method of time lag determination (optimisation of covariance)?

p.2945, l.2: In order to really evaluate the possibilities for chemical reactions within the canopy, it would be useful to include information on chemical and turbulent time scales for the possible processes involved. The trees are not very tall (9m). No information on tree density is given, so it is difficult to assess the possible residence time in trunkspace

and canopy.

p.2945, p.15: It would be useful to include information on the maximum possible deposition velocity (derived from momentum flux) to compare with the deposition velocity given for HNO_3 .

p.2946, l.13: The upward fluxes of HNO_3 in summer are a bit surprising especially considering that the mixing ratios of HNO_3 are higher than in winter. This is explained by in canopy chemistry, which is of course possible, but requires a certain residence time of the air masses to allow for the chemical transformations. As mentioned above some more details about the time scales involved would be useful to understand this possible interpretation of the observed fluxes. Another possibility pathway to consider is re-emission of nitrogen oxides from previously deposited material on needle and stem surfaces (see e.g. Hari et al. 2003 and Zhou et al. 2003).

3 Technical comments

p.2937, l.22: Fig. 4 does not show mixing ratio. There is some mixing up of figures, also on page 2944, l.18 and p. 2945, l.9.

p. 2938, l.19: “title” should be “tilt”

4 References

Hari, P., et al. 2003. Ultraviolet radiation generates NO_x emission from Scots pine shoots. *Nature*, **422**, 134.

Zhou, X. L. et al, 2003. Nitric acid photolysis on surfaces in low- NO_x environments:

Significant atmospheric implications. *Geophysical Research Letters* **30** (23): Art. No. 2217.

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