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Atmospheric
Chemistry
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Discussions

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

**Anonymous Referee #1**

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## 1. General comment

The mechanisms that control nitrogen (N) exchange with ecosystems are still poorly understood, and this is at least in part due to the absence of robust sensors for eddy-covariance flux measurements of these compounds. This is particularly true for organic nitrogen compounds. Although about 30% of wet deposition of N tends to be in organic form (Holland, et al., 1999), very little is known about the sources of this organic fraction. The paper by Farmer et al. makes an important contribution by introducing a new powerful analytical technique suitable for the measurement of surface / atmosphere exchange fluxes and presents very interesting first results. The paper is generally well written and provides a detailed uncertainty analysis of the new technique.

## 2. Major scientific comments

While the proposed technique is fast, it can, regrettably, not distinguish between gas and aerosol phase. This needs to be considered in more detail throughout the manuscript. For example, the authors discuss deposition velocities of nitric acid, while the measured entity almost certainly includes a contribution from ammonium nitrate aerosol.

In addition, I share the concern of the other Interactive Comments on the manuscript, that the reported emission fluxes of nitric acid are highly counter-intuitive. The time-scale analysis indeed suggests that NO2 reaction with OH would be insufficient to explain the fluxes observed. In addition, even in canopies where VOC emissions are considerable, OH has been shown to follow a deposition profile (e.g. ECHO campaign at Julich, Germany). As a consequence, HNO3 formation may in fact be more efficient above the canopy than within the canopy. In general, nitric acid is expected to be deposited at Vmax (= 1/(Ra + Rb)) and should thus have offered the possibility of a powerful validation of the measurement technique.

Nitric acid has been reported to show unexpected behaviour, such as reduced or enhanced deposition, or even emission gradients (e.g. Huebert, et al., 1988, Neftel, et al., 1996, Nemitz, et al., 2004), which has generally been attributed to the dynamics of the NH3-HNO3-NH4NO3 equilibrium. As nitric acid and ammonium nitrate are converted into each other, however, the flux of total nitrate (HNO3 + aerosol NO3-) is conserved. As this is the entity measured by the TD-LIF, this reaction does not provide an explanation for the nitric acid emission reported in this paper. There is some evidence of HNO3 emission from fertilizer application (Sutton, et al., 1998) or from volatilisation of previously deposited NH4NO3, but these effects seem to be unlikely to be important at the low N inputs apparently experienced by Blodgett Forest. Recent measurements by aerosol mass spectrometry, however, have provided some indication that organic nitrate may be an important component of the (presumably) biogenic aerosol formed above the Finnish boreal forest (Allan, et al., 2006). The authors should explore alternative explanations for the HNO3 emissions observed and make sure that these fluxes do not indicate an artifact in the measurements.

3. Minor scientific comments

p 2924, l 17. The discussion is correct for semi-natural ecosystems. However, in general nitrogen may also enter ecosystems as fertilizer.

P 2924, l 20 & p 2928, l 7 & p 2944, l 22. The existence of a physiological compensation point for NO2 has been discussed controversially in the literature and may, in fact, represent chemical effects. Is there any indication from the measurements reported in this paper that the NO2 flux switches sign at a defined air concentration?

P 2924, l 25. The effects of N on the green house gas budget of an ecosystem are in fact very complex. Increased N deposition may also stimulate the emission of N2O and may have positive effects on soil respiration, partly offsetting the increase in photosynthesis.

P 2925, l 9. The Holland et al. (2005) reference mainly points to inferential modeling of N dry deposition, while there is a whole body of literature that has directly measured N dry deposition, including that of ammonia.

P 2926, l 22. Other references for HNO3 emission (or fast deposition) due to flux divergence include: Brost, et al., 1988, Neftel, et al., 1996, Van Oss, et al., 1998, Zhang, et al., 1995.

P 2927, l 9. I would like to draw the authors' attention to a recent paper by Turnipseed et al. (2006), which reports eddy-covariance flux measurements of PAN, MPAN and PPN, suggesting that these compounds deposit much faster than predicted by current models, especially to wet surfaces. The authors may want to work these results into

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their discussion.

P 2928, l 23. At 3 m above a 9 m canopy, the measurements were made well within the surface roughness layer and not in the inertial sublayer. This should be borne in mind when interpreting the power spectral analysis as it could cause deviations from the -5/3 and -4/3 slopes.

P 2929, l 19. The statement that detection of ammonium nitrate has been demonstrated is rather qualitative. At what efficiency was it detected? Similarly, ‘may be measured’ should probably replaced by ‘are measured’.

P 2932, l 2. The inlet temperature of 60°C is probably already sufficient to volatilize a significant proportion of the ammonium nitrate aerosol?

P 2932, l 23. The text states here that the sensor separation was 30 cm (0.3 m in SI units!), while later in the manuscript flux losses are calculated for a sensor separation of 20 cm.

P 2934, l 16 & P 2939, l 18. I understand that there were physical reasons for the time lag to change with time, but I do not fully understand the reason for time lags differing between 1.6 and 3 s between channels. In support of the comments by Neftel et al., I would suggest recalculating fluxes using a ’typical’ time lag or a generalized relationship between the time lag and other variables (e.g. T and P) to avoid biasing the fluxes by looking for the absolute maximum in the correlation.

P 2935, l 9. Do these concentration ranges indicate the absolute ranges or ‘typical’ ranges? Fig. 9 suggests that negative HNO3 concentrations were also derived (and should be reported and shown in Fig. 9 to give a full impression of the uncertainties). I suggest adding a table on concentrations statistics listing parameters such as absolute minimum, maximum, 5 and 95%-iles, arithmetic mean, median, together with arithmetic and geometric standard deviations.

P 2936. l 8. I believe the stationarity test applied in this manuscript goes back to Foken

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and Wichura (1996), which may be the more direct reference to use here?

P 2936, l 23. Although not focus of this study, NO (which also forms part of NOy) is biologically controlled.

P 2937, l 25. The list of reasons of systematic errors appears to be inconsistent: time lag correction is dealt with earlier in the manuscript, while sensor separation is one of the reasons for damping of high frequency fluctuations. Maybe the authors should list reasons for damping instead: sensor separation, smoothing in inlet lines, limitations in sensor response time etc.

P 2938, l 11-14. How was the underestimation due to sensor separation evaluated? Eq. (5) is a formulation for a single frequency (f). Was a measured or ideal power spectrum used to evaluate loss for the total flux?

P 2939, l 10. The flux loss due to the half-power damping frequency of the sampling tube (6 Hz) of 2 to 7% appears to be large compared with the flux loss attributed to the response time (tau = 0.6 s corresponding to f = 1.7 Hz) of the sensor itself of 3.6%. Maybe I misunderstand the authors?

P 2942. Flux units of ppb m / s are not very intuitive. I would like to encourage the authors to consider using umol m-2 s-1 or ug m-2 s-1 instead.

P 2944, l 18. The reference to Fig. 4 does not appear to make sense here as the winter fluxes are discussed.

P 2945, l 7. I think it is highly unlikely that the tower would actually remove sticky gases at a noticeable rate. It is potentially possible that it leads to flux losses associated with flow distortion, though. However, reduced turbulence at night is the most likely cause for smaller fluxes. Deposition fluxes are well known to be reduced when aerodynamic and laminar sub-layer resistances are large. Similarly, emission that is governed by compensation points may be suppressed in conditions of low turbulence, as air concentrations near the ground are larger when turbulence is low, with a negative feedback on further emission.

P 2945, l 24. I guess the word ‘integrated’ should be dropped as the winter flux is calculated as the product of the average flux and the 90 day period.

P 2946. In the discussion of annual N deposition estimates, it is not clear which figures include reduced N and organic N and which estimate relate only to oxidized N. At such low total N deposition, dry deposition of ammonia could make an important contribution to total N deposition. Similarly, the wet deposition estimates may include ammonium. Could the authors please clarify.

P 2946, l 19. Are there any NO soil emission measurements available for Blodgett forest? It would be very interesting to compare NO2 emissions with measured or estimated NO soil emissions.

P 2947, l 14. The authors carefully derive a bias of $<$ 3.5% and a random error due to the instrument of 10%. Studies have shown that even momentum fluxes can easily differ by 20% between ultrasonic anemometers, especially at low turbulence, due to measurement uncertainties, errors in the co-ordinate rotation and spatial and temporal variability in the turbulence. Hence, the errors presented here need to be put into perspective.

4. Technical comments

General: all symbols should be printed in italics. The ‘*’ of u* should be a subscript.

P 2925, l 9. ‘Bytnerowicz et al., 1996’ should read ‘Bytnerowicz and Fenn, 1996’, according to the literature list.

P 2926, l 8. I suggest to improve the English: “Model results by Munger et al. (1998) indicate that deposition Ě”

P 2937, l 7. ‘shows’

P 2937, l 22. Should ‘figure 3’ refer to ‘figure 2’ instead?

P2945, l 9. Here ‘Fig. 3’ should refer to Fig. 4.

Fig. 1. The line styles in the caption do not match the line styles in the figure.

Fig. 3. The graph indicates a time lag of approximately 1.7 s and not 2.2 s as stated in the text.

Figs. 4 & 9. Please increase the font size of the axis and tick labels.

Fig. 4. Surely, the units of the fluxes are mmol /m2/hr1 as in Fig. 9?

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